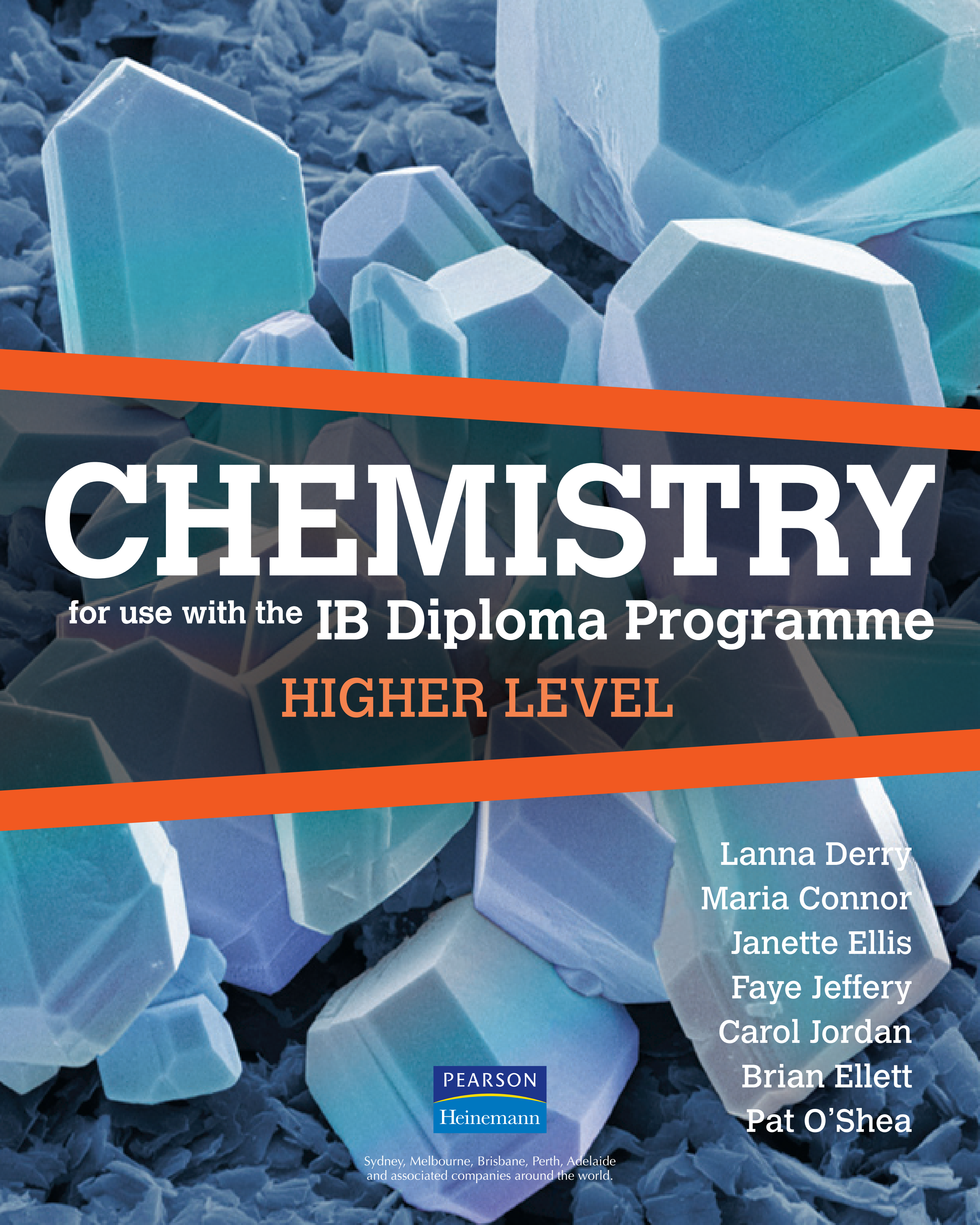

CHEMISTRY

for use with the IB Diploma Programme

HIGHER LEVEL

Lanna Derry
Maria Connor
Janette Ellis
Faye Jeffery
Carol Jordan
Brian Ellett
Pat O'Shea

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for use with the IB Diploma Programme

HIGHER LEVEL

The complete chemistry package

CHEMISTRY: For use with the IB Diploma Programme Higher Level is the most comprehensive chemistry text specifically written for the IB Diploma Programme Chemistry course, Higher Level.

The content is easy to follow and provides regular opportunities for revision and consolidation. All assessment statements of the IB Diploma Programme Chemistry syllabus are covered in highly structured and meaningful ways.

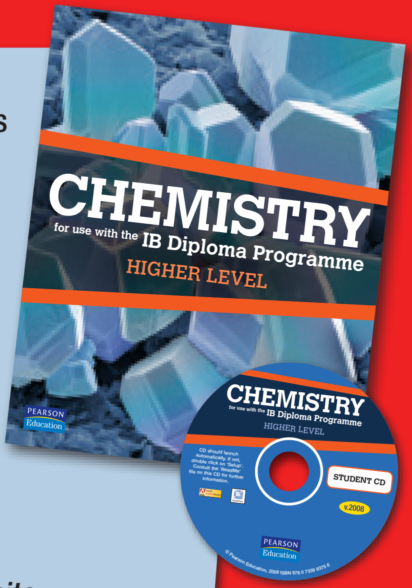
Coursebook includes Student CD

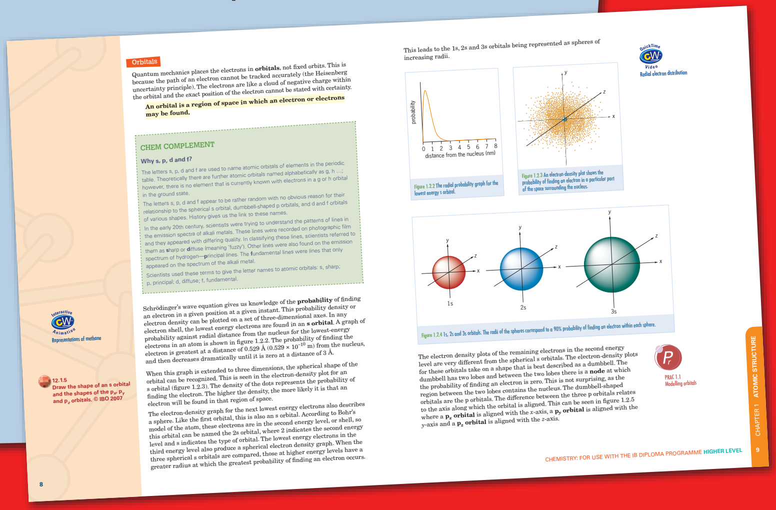
Each chapter in the coursebook includes:

- focus on the IB Additional Higher Level (AHL) Diploma Programme Chemistry syllabus, topics 12 to 20
- Syllabus Assessment Statements given beside the relevant theory
- stimulating photos and full colour illustrations to support learning of chemical concepts
- theory broken into manageable chunks for ease of learning
- comprehensive exercises for ongoing review and consolidation
- **Chem Complement** boxes, which engage students with interesting extension material and applications to Aims 8 and 9 for Experimental Sciences
- **Theory of Knowledge** boxes, which allow easy integration of this requirement of the syllabus
- ICT activities, which address Aim 7 for Experimental Sciences and are available on the *Companion Website*
- **Chapter summary**, which includes chapter glossary and key points
- **Review questions** to revise all chapter content
- **Comprehensive topic test** of examination questions.

Student CD contains:

- an electronic version of the coursebook
- fully worked solutions to all coursebook questions
- a link to the live *Companion Website.*





Orbitals

Quantum mechanics places the electrons in **orbitals**, not fixed orbits. This is because the path of an electron cannot be tracked accurately (the Heisenberg uncertainty principle). The electrons are like a cloud of negative charge within the orbital and the exact position of the electron cannot be stated with certainty.

An orbital is a region of space in which an electron or electrons may be found.

CHEM COMPLEMENT

Why s, p, d and f?

The letters s, p, d and f are used to name atomic orbitals of elements in the periodic table. Theoretically there are further atomic orbitals named alphabetically as g, h …; however, there is no element that is currently known with electrons in a g or h orbital in the ground state.

The letters s, p, d and f appear to be rather random with no obvious reason for their relationship to the spherical s orbital, dumbbell-shaped p orbitals, and d and f orbitals of various shapes. History gives us the link to these names.

In the early 20th century, scientists were trying to understand the patterns of lines in the emission spectra of alkali metals. These lines were recorded on photographic film and they appeared with differing quality. In classifying these lines, scientists referred to them as **s**harp or **d**iffuse (meaning 'fuzzy'). Other lines were also found on the emission spectrum of hydrogen—**p**rincipal lines. The **f**undamental lines were lines that only appeared on the spectrum of the alkali metal.

Scientists used these terms to give the letter names to atomic orbitals: s, sharp; p, principal; d, diffuse; f, fundamental.

Schrödinger's wave equation gives us knowledge of the **probability** of finding an electron in a given position at a given instant. This probability density or electron density can be plotted on a set of three-dimensional axes. In any electron shell, the lowest energy electrons are found in an **s orbital**. A graph of probability against radial distance from the nucleus for the lowest-energy electrons in an atom is shown in figure 1.2.2. The probability of finding the electron is greatest at a distance of 0.529 Å (0.529 × 10^{-10} m) from the nucleus, and then decreases dramatically until it is zero at a distance of 3 Å.

When this graph is extended to three dimensions, the spherical shape of the orbital can be recognized. This is seen in the electron-density plot for an s orbital (figure 1.2.3). The density of the dots represents the probability of finding the electron. The higher the density, the more likely it is that an electron will be found in that region of space.

The electron-density graph for the next lowest energy electrons also describes a sphere. Like the first orbital, this is also an s orbital. According to Bohr's model of the atom, these electrons are in the second energy level, or shell, so this orbital can be named the 2s orbital, where 2 indicates the second energy level and s indicates the type of orbital. The lowest energy electrons in the third energy level also produce a spherical electron density graph. When the three spherical s orbitals are compared, those at higher energy levels have a greater radius at which the greatest probability of finding an electron occurs.

Interactive CW Animation
Representations of methane

12.1.5
Draw the shape of an s orbital and the shapes of the p_x, p_y and p_z orbitals. © IBO 2007

8

This leads to the 1s, 2s and 3s orbitals being represented as spheres of increasing radii.

QuickTime CW Video
Radial electron distribution

Figure 1.2.2 The radial probability graph for the lowest energy s orbital.

Figure 1.2.3 An electron-density plot shows the probability of finding an electron in a particular part of the space surrounding the nucleus.

Figure 1.2.4 1s, 2s and 3s orbitals. The radii of the spheres correspond to a 90% probability of finding an electron within each sphere.

The electron density plots of the remaining electrons in the second energy level are very different from the spherical s orbitals. The electron-density plots for these orbitals take on a shape that is best described as a dumbbell. The dumbbell has two lobes and between the two lobes there is a **node** at which the probability of finding an electron is zero. This is not surprising, as the region between the two lobes contains the nucleus. The dumbbell-shaped orbitals are the p orbitals. The difference between the three p orbitals relates to the axis along which the orbital is aligned. This can be seen in figure 1.2.5 where a $\mathbf{p_x}$ **orbital** is aligned with the x-axis, a $\mathbf{p_y}$ **orbital** is aligned with the y-axis and a $\mathbf{p_z}$ **orbital** is aligned with the z-axis.

PRAC 1.1
Modelling orbitals

CHAPTER 1 ATOMIC STRUCTURE

CHEMISTRY: FOR USE WITH THE IB DIPLOMA PROGRAMME HIGHER LEVEL 9

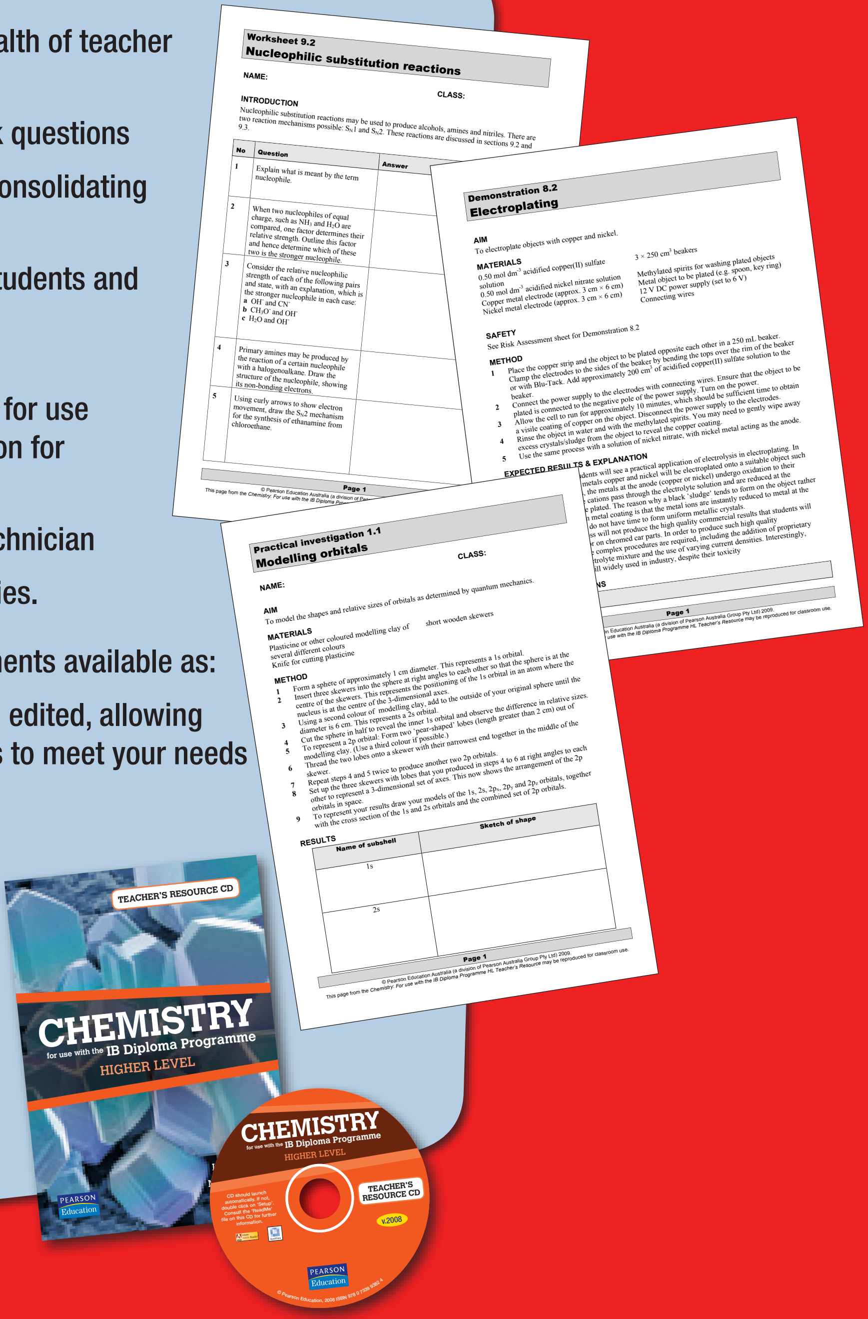
Teacher's Resource CD

The *Teacher's Resource CD* provides a wealth of teacher support material, including:

- **fully worked solutions** to coursebook questions
- **worksheets** for practising skills and consolidating theory; answers are also included
- **teacher demonstrations** to engage students and enhance understanding of concepts
- **practical investigations** to enhance the learning of chemical concepts and for use in meeting the mandated time allocation for practical work
- **practical notes** for the teacher/lab technician
- **risk assessments** for practical activities.

This time-saving resource contains documents available as:

- Microsoft Word documents that can be edited, allowing you to modify and adapt any resources to meet your needs
- PDFs to make printing easy.



Worksheet 9.2
Nucleophilic substitution reactions

NAME:

CLASS:

INTRODUCTION

Nucleophilic substitution reactions may be used to produce alcohols, amines and nitriles. There are two reaction mechanisms possible: S_N1 and S_N2. These reactions are discussed in sections 9.2 and 9.3.

No	Question	Answer
1	Explain what is meant by the term nucleophile.	
2	When two nucleophiles of equal charge, such as NH_3 and H_2O are compared, one factor determines their relative strength. Outline this factor and hence determine which of these two is the stronger nucleophile.	
3	Consider the relative nucleophilic strength of each of the following pairs and state, with an explanation, which is the stronger nucleophile in each case: **a** OH^- and CN^- **b** CH_3O^- and OH^- **c** H_2O and OH^-	
4	Primary amines may be produced by the reaction of a certain nucleophile with a halogenoalkane. Draw the structure of the nucleophile, showing its non-bonding electrons.	
5	Using curly arrows to show electron movement, draw the S_N2 mechanism for the synthesis of ethanamine from chloroethane.	

Page 1

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Demonstration 8.2
Electroplating

AIM
To electroplate objects with copper and nickel.

MATERIALS

0.50 mol dm^{-3} acidified copper(II) sulfate solution	3 × 250 cm^3 beakers
0.50 mol dm^{-3} acidified nickel nitrate solution	Methylated spirits for washing plated objects
Copper metal electrode (approx. 3 cm × 6 cm)	Metal object to be plated (e.g. spoon, key ring)
Nickel metal electrode (approx. 3 cm × 6 cm)	12 V DC power supply (set to 6 V)
	Connecting wires

SAFETY
See Risk Assessment sheet for Demonstration 8.2

METHOD
1 Place the copper strip and the object to be plated opposite each other in a 250 mL beaker. Clamp the electrodes to the sides of the beaker by bending the tops over the rim of the beaker or with Blu-Tack. Add approximately 200 cm^3 of acidified copper(II) sulfate solution to the beaker.
2 Connect the power supply to the electrodes with connecting wires. Ensure that the object to be plated is connected to the negative pole of the power supply. Turn on the power.
3 Allow the cell to run for approximately 10 minutes, which should be sufficient time to obtain a visile coating of copper on the object. Disconnect the power supply to the electrodes.
4 Rinse the object in water and with the methylated spirits. You may need to gently wipe away excess crystals/sludge from the object to reveal the copper coating.
5 Use the same process with a solution of nickel nitrate, with nickel metal acting as the anode.

EXPECTED RESULTS & EXPLANATION
udents will see a practical application of electrolysis in electroplating. In
metals copper and nickel will be electroplated onto a suitable object such
, the metals at the anode (copper or nickel) undergo oxidation to their
cations pass through the electrolyte solution and are reduced at the
e plated. The reason why a black 'sludge' tends to form on the object rather
n metal coating is that the metal ions are instantly reduced to metal at the
do not have time to form uniform metallic crystals.
ss will not produce the high quality commercial results that students will
r on chromed car parts. In order to produce such high quality
e complex procedures are required, including the addition of proprietary
trolyte mixture and the use of varying current densities. Interestingly,
ill widely used in industry, despite their toxicity

NS

Page 1
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Practical investigation 1.1
Modelling orbitals

CLASS:

NAME:

AIM
To model the shapes and relative sizes of orbitals as determined by quantum mechanics.

MATERIALS

Plasticine or other coloured modelling clay of several different colours	short wooden skewers
Knife for cutting plasticine	

METHOD
1 Form a sphere of approximately 1 cm diameter. This represents a 1s orbital.
2 Insert three skewers into the sphere at right angles to each other so that the sphere is at the centre of the skewers. This represents the positioning of the 1s orbital in an atom where the nucleus is at the centre of the 3-dimensional axes.
3 Using a second colour of modelling clay, add to the outside of your original sphere until the diameter is 6 cm. This represents a 2s orbital.
4 Cut the sphere in half to reveal the inner 1s orbital and observe the difference in relative sizes.
5 To represent a 2p orbital: Form two 'pear-shaped' lobes (length greater than 2 cm) out of modelling clay. (Use a third colour if possible.)
6 Thread the two lobes onto a skewer with their narrowest end together in the middle of the skewer.
7 Repeat steps 4 and 5 twice to produce another two 2p orbitals.
8 Set up the three skewers with lobes that you produced in steps 4 to 6 at right angles to each other to represent a 3-dimensional set of axes. This now shows the arrangement of the 2p orbitals in space.
9 To represent your results draw your models of the 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals, together with the cross section of the 1s and 2s orbitals and the combined set of 2p orbitals.

RESULTS

Name of subshell	Sketch of shape
1s	
2s	

Page 1

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Companion Website

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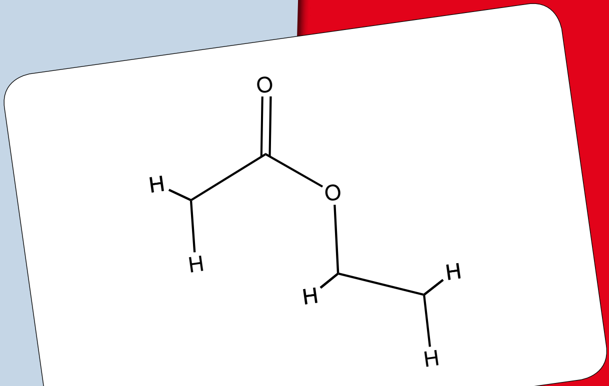
The *Companion Website* addresses Aim 7 for Experimental Sciences by providing easy integration of technology into the classroom. It contains a wealth of support material for students and teachers to enhance teaching and learning in chemistry.

The interactive material on the *Companion Website* allows students to review their work and revise fundamental concepts, as well as providing an opportunity for accelerated learning.

The *Companion Website* contains:

- **Review Questions**—auto-correcting multiple-choice questions for exam revision
- **Interactive Animations**—to engage students in exploring concepts
- **QuickTime Videos**—to explore chemical concepts in a visually stimulating way
- **3D Molecules Gallery**—for interactive viewing and manipulating of molecular structures
- **Web Destinations**—a list of reviewed websites that support further investigation and revision.



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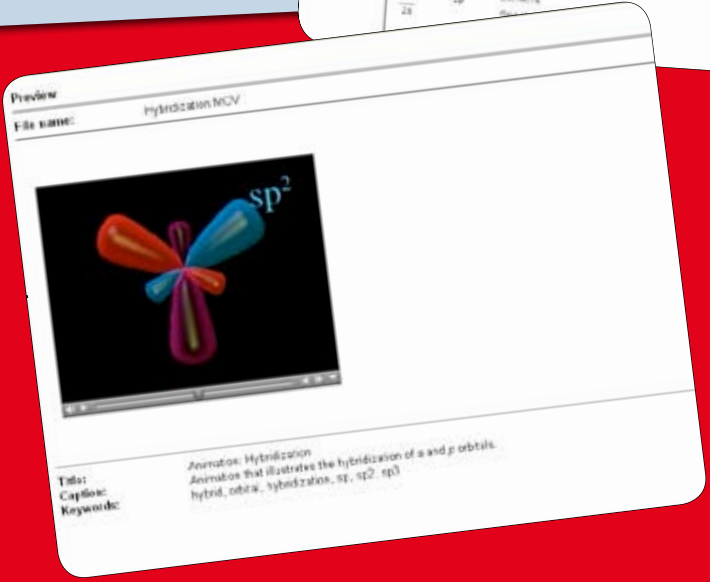

File name: Hybridization.MOV

Title: Animation: Hybridization
Caption: Animation that illustrates the hybridization of s and p orbitals.
Keywords: hybrid, orbital, hybridization, sp, sp2, sp3

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visit www.pearsoned.com.au/schools

MEET THE AUTHORS

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Lanna Derry, the lead author of the *CHEMISTRY: For use with the IB Diploma Programme* series, is a highly experienced teacher of IB Chemistry. She has taught senior Chemistry in independent schools for more than twenty years and has authored revision guides for Year 12 Chemistry. Lanna is currently teaching IB Chemistry at Tintern Girls Grammar School, Ringwood East, Victoria, Australia.

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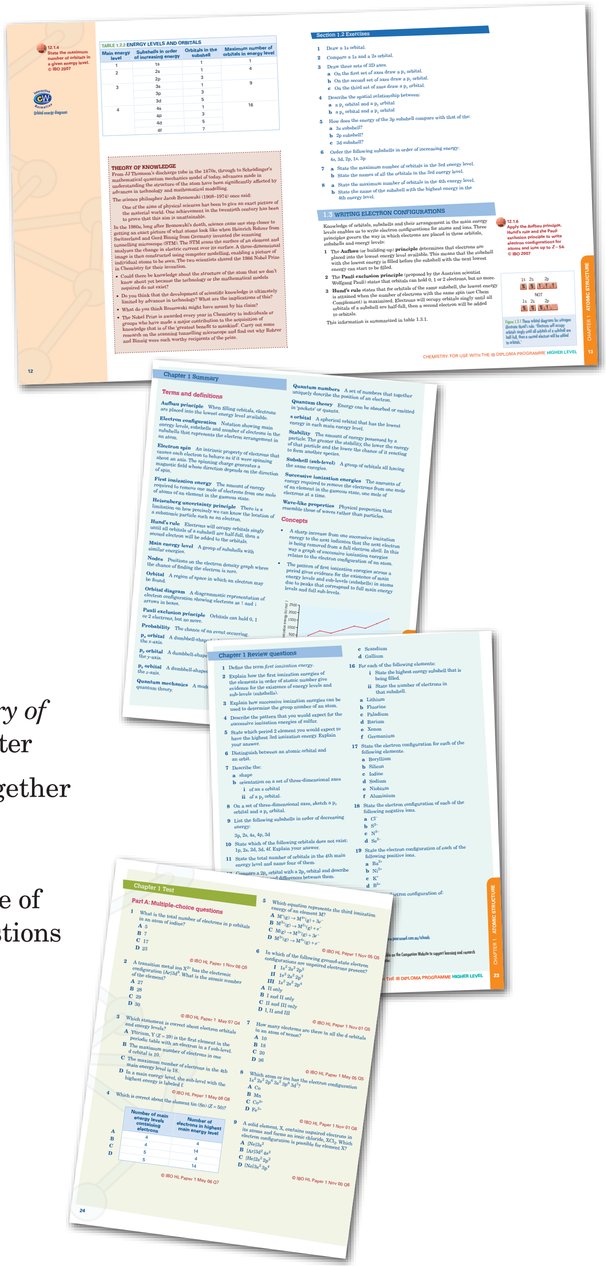
Pat O’Shea is a highly experienced teacher of Chemistry. He is currently Deputy Principal at Loreto College, Ballarat, Victoria, Australia. Pat has presented at many workshops for senior Chemistry teachers.

HOW TO USE THIS BOOK

Our aim has been to present chemistry as exciting, accessible and relevant. The content is carefully structured with regular opportunities for revision and consolidation to prepare students for the IB Diploma Programme Higher Level Chemistry examinations.

Major features

- *Chapter opening pages* that include a stimulating photo and a simple, student-friendly syllabus-related list of what students should be able to do by the end of the chapter
- **Chem Complement** boxes that engage students with interesting extensions of the Chemistry theory and applications to Aims 8 and 9 for Experimental Sciences
- **Theory of Knowledge** boxes that address the links between the syllabus and aspects of the scientific way of knowing as required by the syllabus
- *ICT activities* that address Aim 7 for Experimental Sciences and are available on the Companion Website
- *Comprehensive exercises* that encourage students to consolidate their learning in a systematic manner while familiarising students with the IB command terms
- *Glossary of terms* and a *summary of concepts* at the end of each chapter
- *Review questions* that draw together all aspects of the topic
- *End-of-chapter tests* that allow students to test their knowledge of the topic thoroughly using questions from past IBO examinations



Icons in the coursebook

- **Assessment Statement** icons denote Assessment Statements from the IB Diploma Programme Additional Higher Level Chemistry syllabus.
- **Worksheet** icons denote when a worksheet giving extra practice on a key part of the topic is available. These can be found on the **Teacher's Resource CD**.
- **Prac** icons denote when a practical investigation is available. These can be found on the **Teacher's Resource CD**.
- **Demo** icons denote when a teacher demonstration is available. These can be found in the **Teacher's Resource CD**.
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- **Companion Website—Review Questions** icons denote when multiple-choice review questions are available to support revision. These can be accessed on the Companion Website.

Other features

- **Worked examples** of calculations and chemical structures to aid mastery of difficult concepts
- **Glossary** at the end of the text as well as at the end of each chapter
- **Periodic table** with relative atomic masses included on the inside front cover to provide a quick and easy reference
- **Appendices** including relevant thermochemical data and acid and base dissociation contants

Student CD

This interactive resource contains:

- an electronic version of the coursebook
- fully worked solutions (including diagrams) to all coursebook questions
- a link to the live Companion Website (Internet access required) to provide access to course-related Web links.

Other components

- Companion Website www.pearsoned.com.au/schools
- Teacher's Resource CD

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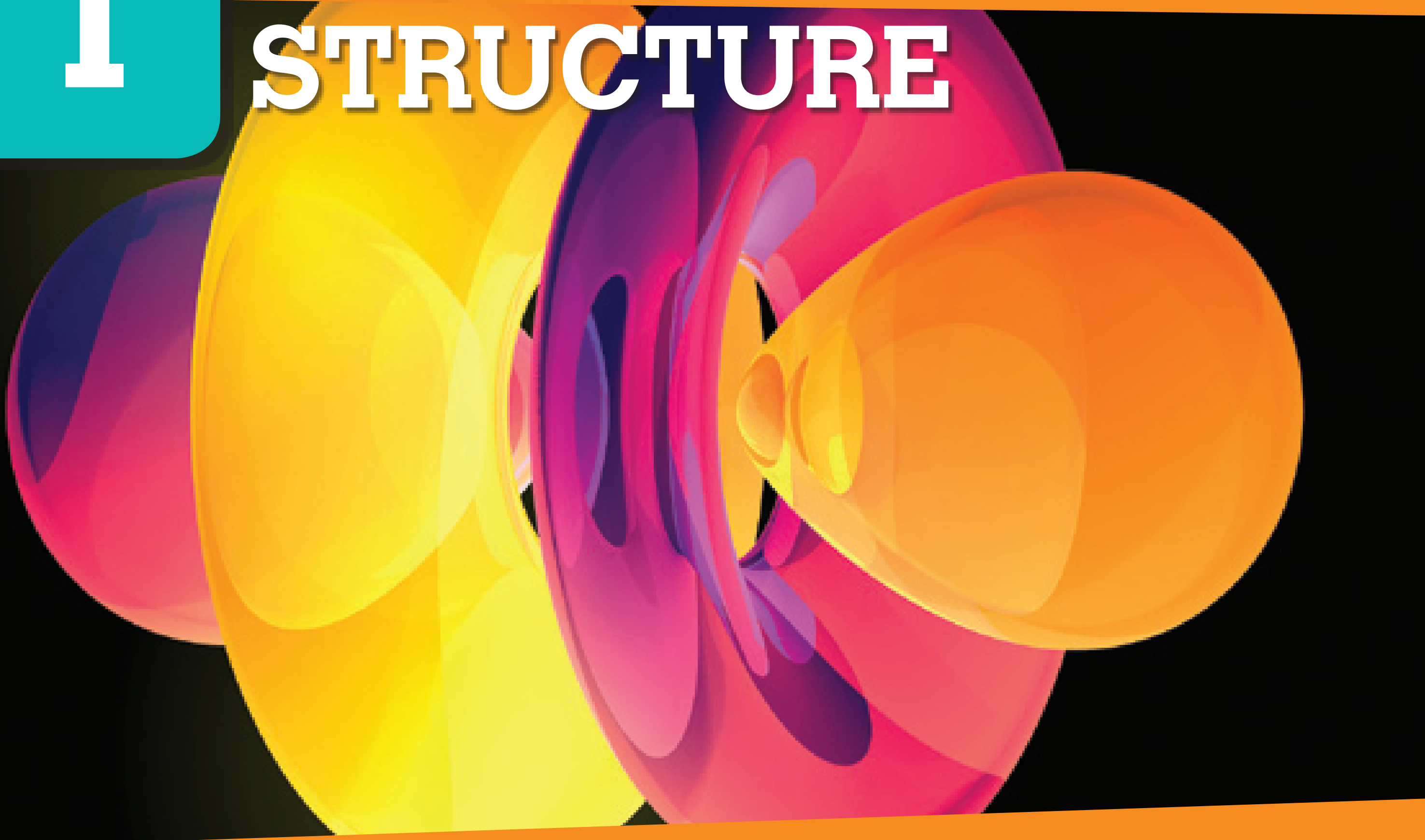
1

ATOMIC STRUCTURE



Chapter overview

This chapter covers the IB Chemistry syllabus Topic 12: Atomic Structure.

By the end of this chapter, students should be able to:

- explain how successive ionization energies relate to the electron configuration of an atom
- explain how the pattern in first ionization energies across a period gives evidence for the existence of main energy levels and sub-levels in atoms
- define the terms *orbital*, *subshell* (sub-level) and *shell* (main energy level)
- state the relative energies of the s, p, d and f subshells in a main energy level
- draw the shape of an s orbital and the shapes of the p_x, p_y and p_z orbitals
- use the periodic table to determine electron configurations for atoms up to $Z = 54$
- state the Aufbau principle, Hund's rule and the Pauli exclusion principle
- write electron configurations for atoms and ions up to $Z = 54$.

IBO Assessment statements 12.1.1 to 12.1.6

THE STORY SO FAR …

In 1900 the German physicist Max Planck was the first to apply **quantum theory** to a physical problem. His theory related to the radiation released by a body at high temperature. Planck discovered that the theoretical formula he had devised to explain this phenomenon required acceptance of what was then a radical assumption that energy was only released in distinct ‘chunks’ or quanta. In 1913, Niels Bohr applied Planck’s theory in his explanation of atomic structure.

The problem with atomic theory up until that time was that classical physics could not explain the then current (Rutherford’s) model, which suggested that electrons spiralled around the nucleus in a series of orbits. If atoms obeyed the laws of classical physics, the energy they radiated would ultimately run out and they would collapse into the nucleus.

Bohr used quantum theory to explain the behaviour of electrons around a nucleus. Electrons only existed in ‘fixed’ orbits or energy levels where they did not radiate energy. The energy levels could be assigned **quantum numbers** 1, 2, 3 etc. Energy would only be radiated if the electrons moved between a higher energy orbit and a lower energy orbit. Bohr’s application of his theory to hydrogen atoms matched physical observations. His predictions of the wavelengths of light that hydrogen atoms should release when electrons moved between orbits also matched physical observations—information that further validated quantum theory.

1.1 IONIZATION ENERGIES AND ELECTRON ARRANGEMENTS

You will recall from your study of standard level topic 3 that the **first ionization energy** is the amount of energy required to remove one mole of electrons from one mole of atoms of an element in the gaseous state (*Chemistry: For use with the IB Diploma Programme Standard Level,* p. 82). Similarly the **successive ionization energies** of an element are the amounts of energy required to remove all the electrons from one mole of an element in the gaseous state, one mole of electrons at a time.

Successive ionization energies

If an electron has energy equal to or greater than that of the highest possible energy level of the atom, it will leave the atom and a positive ion will be formed. Electrons in energy levels that are further from the nucleus have higher energy than those that are closer to the nucleus; therefore, it is these electrons that can be removed more easily by the addition of energy. The first electrons to be removed by the addition of energy will be those that already have the highest energy—those in the valence electron shell (see figure 1.1.1). This can also be explained in terms of the attraction of the electrons to the nucleus. As electrons in the valence shell are furthest from the nucleus, they are not attracted to it as strongly as electrons in other electron shells, and so they will be the ones that are removed first.

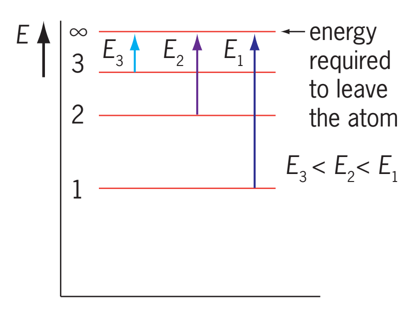


Figure 1.1.1 Electrons in higher energy levels need to gain less extra energy in order to leave the atom.

The first electron to be removed is one that already has a high energy and is least strongly attracted to the nucleus; that is, one in the valence shell. This will require the lowest ionization energy. If there are more electrons in this outer shell, then they will be removed next, with the ionization energy gradually increasing. When the outermost electron shell is empty, the next electron to be lost will come from the next closest shell to the nucleus. But since this shell is full, and therefore stable, a great deal more energy will be required to remove one electron from this shell than was needed to remove the previous electron.

AS **12.1.2 Explain how successive ionization energy data is related to the electron configuration of an atom. © IBO 2007**

The pattern formed by the successive ionization energies of an atom provides evidence for the existence of energy levels around the nucleus and allows us to work out the **electron configuration** of an atom.

Consider the successive ionization energies for nitrogen and magnesium below:

TABLE 1.1.1 SUCCESSIVE IONIZATION ENERGIES FOR NITROGEN

Ionization	Ionization energy (kJ mol^{-1})
$N(g) \rightarrow N^{+}(g) + e^{-}$	I_1 = 1400
$N^{+}(g) \rightarrow N^{2+}(g) + e^{-}$	I_2 = 2856
$N^{2+}(g) \rightarrow N^{3+}(g) + e^{-}$	I_3 = 4578
$N^{3+}(g) \rightarrow N^{4+}(g) + e^{-}$	I_4 = 7475
$N^{4+}(g) \rightarrow N^{5+}(g) + e^{-}$	I_5 = 9440
$N^{5+}(g) \rightarrow N^{6+}(g) + e^{-}$	I_6 = 53 266
$N^{6+}(g) \rightarrow N^{7+}(g) + e^{-}$	I_7 = 64 358

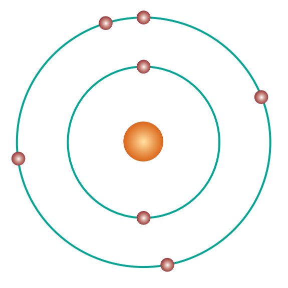


Figure 1.1.2 An atom of nitrogen has 5 electrons in its 2nd electron shell and 2 electrons in the 1st electron shell.

You will notice in table 1.1.1 that the first five ionization energies gradually increase from 1400 kJ mol^{-1} to 9440 kJ mol^{-1}, then the 6th ionization energy is equal to 53 266 kJ mol^{-1}. This large increase indicates that the 6th electron to be removed is coming from the next energy level, which is full and closer to the nucleus. A much greater amount of energy is needed to remove one electron from this new energy level than from the previous energy level because the electrons are experiencing a significantly larger attraction to the nucleus. This leads us to the electron configuration of 2,5 for nitrogen.

A similar trend can be seen for the successive ionization energies of magnesium.

TABLE 1.1.2 SUCCESSIVE IONIZATION ENERGIES FOR MAGNESIUM

Ionization	Ionization energy (kJ mol^{-1})	Ionization	Ionization energy (kJ mol^{-1})
$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$	I_1 = 736	$Mg^{6+}(g) \rightarrow Mg^{7+}(g) + e^{-}$	I_7 = 21 703
$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$	I_2 = 1451	$Mg^{7+}(g) \rightarrow Mg^{8+}(g) + e^{-}$	I_8 = 25 656
$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-}$	I_3 = 7733	$Mg^{8+}(g) \rightarrow Mg^{9+}(g) + e^{-}$	I_9 = 31 642
$Mg^{3+}(g) \rightarrow Mg^{4+}(g) + e^{-}$	I_4 = 10 540	$Mg^{9+}(g) \rightarrow Mg^{10+}(g) + e^{-}$	I_{10} = 35 461
$Mg^{4+}(g) \rightarrow Mg^{5+}(g) + e^{-}$	I_5 = 13 630	$Mg^{10+}(g) \rightarrow Mg^{11+}(g) + e^{-}$	I_{11} = 169 987
$Mg^{5+}(g) \rightarrow Mg^{6+}(g) + e^{-}$	I_6 = 17 995	$Mg^{11+}(g) \rightarrow Mg^{12+}(g) + e^{-}$	I_{12} = 189 363

The first two successive ionization energies of magnesium increase from 736 kJ mol^{-1} to 1451 kJ mol^{-1}. The next ionization energy increases greatly to 7732.6 kJ mol^{-1}, indicating that the 3rd electron is being removed from the next energy level. This energy level is full and closer to the nucleus, so a much greater amount of energy is required for the 3rd electron to be removed than for the 2nd electron. The successive ionization energies increase gradually as electrons are removed from the second electron shell. There is another large jump from 35 461 kJ mol^{-1} for the 10th ionization energy to 169 987 kJ mol^{-1} for the 11th ionization energy, indicating that this electron is being removed from the next energy level, the inner electron shell. This leads us to the electron configuration of 2,8,2 for magnesium.

The pattern formed by successive ionization energies can be seen clearly in a graph of electron being removed against ionization energy (kJ mol^{-1}). Figure 1.1.3 shows the successive ionization energies of nitrogen ($Z = 7$). In figure 1.1.3, the ionization energies for the first 5 electrons are low, suggesting that there are five electrons in the outer shell, then there is a sharp increase in the ionization energies for the 6th and 7th electrons, which are in the first electron shell.

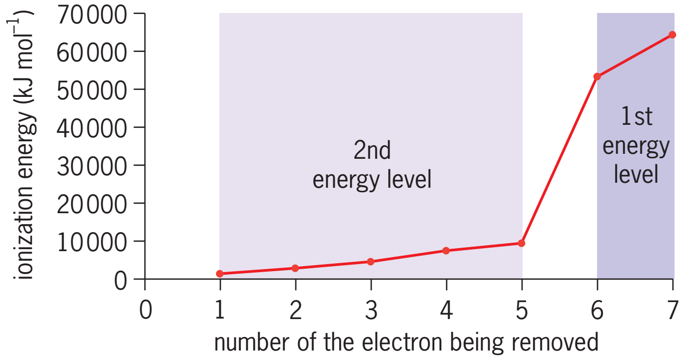


Figure 1.1.3 The successive ionization energies of nitrogen.

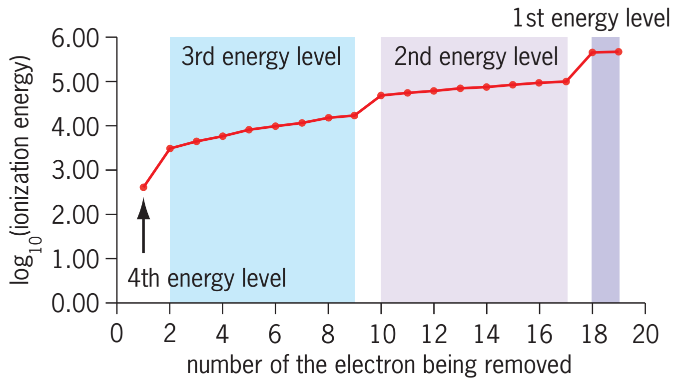


Figure 1.1.4 The successive ionization energies of potassium. This graph is plotted as log$_{10}$(ionization energy), to make the increases more obvious.

Evidence for the four electron shells of potassium can be seen in figure 1.1.4. In this graph there are three sharp increases in ionization energy. The first occurs after 1 electron has been removed and the second and third each after another 8 electrons have been removed. This leads to the electron configuration of 2,8,8,1 for potassium.

Table 1.1.3 shows that the successive ionization energies for the elements of period 3, Na to Ar, increase gradually until the next electron to be removed is from an electron shell that is full. This is shown by the shaded region of the table. When an electron is removed from a full electron shell, the ionization energy increases dramatically.

TABLE 1.1.3 VALUES OF SUCCESSIVE IONIZATION ENERGIES, I_n, (kJ mol^{-1}) FOR THE ELEMENTS OF PERIOD 3

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7	I_8	I_9
Na	494	4562	6912	9543	13353	16610	20114	25490	28933
Mg	736	1451	7733	10540	13630	17995	21703	25656	31642
Al	577	1817	2745	11575	14839	18376	23293	27457	31857
Si	786	1577	3231	4356	16091	19784	23786	29252	33876
P	1060	1903	2912	4956	6273	21268	25397	29854	35867
S	1000	2251	3361	4564	7013	8495	27106	31669	36578
Cl	1260	2297	3826	5158	6540	9362	11020	33610	38600
Ar	1520	2666	3928	5770	7238	8811	12021	13844	40759

First ionization energies

Recall that the first ionization energy of an element is the amount of energy required to remove one mole of electrons from one mole of atoms of an element in the *gaseous* state. The state of the element is important because if the element was solid or liquid, the input of energy would change its state before electrons could be removed. A graph of first ionization energies of the first 54 elements shows distinct patterns that lead us to a greater understanding of the electron structure of an atom.

WORKSHEET 1.1
Ionization energies

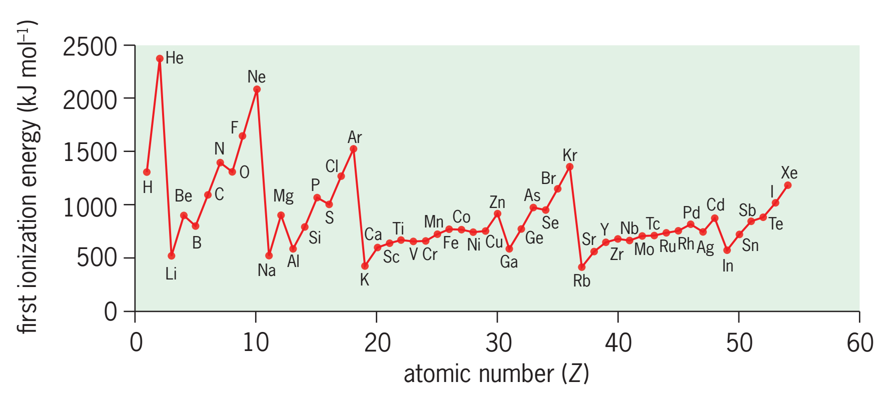


Figure 1.1.5 The first ionization energies of hydrogen to xenon.

The most obvious feature of this graph is the periodic series of peaks corresponding to the first ionization energy of the noble gases (He, Ne, Ar, Kr, Xe). These elements have high first ionization energies because they have a full electron shell and an associated high degree of energetic **stability**. The next most obvious feature of the graph is the lowest point of each periodic series. These troughs correspond to the group 1 elements (Li, Na, K, Rb). These elements have only one electron in the outer shell and so the first ionization energy is small, as little energy is required to remove this electron from the atom. Recall that the attraction between the valence electrons and the nucleus is not great due to the low core charge *(Chemistry: For use with the IB Diploma Programme Standard Level,* p. 85).

12.1.1
Explain how evidence from first ionization energies across periods accounts for the existence of main energy levels and sub-levels in atoms.
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THEORY OF KNOWLEDGE

Both direct and indirect evidence are used to explain the nature of matter. Direct evidence comes from observations and experimentation, while indirect evidence comes from inductive reasoning; that is, by looking at the evidence provided by established laws and theories and using them to draw conclusions and offer explanations. As an IB Chemistry student you can't observe electrons in energy levels or experimentally determine successive ionization energies, but you can interpret the work of scientists such as Bohr, Heisenberg and Schrödinger, and use ionization energy data to provide evidence for the existence of electrons in energy levels.

- Describe examples of knowledge you acquired in Chemistry using direct and indirect evidence.
- Compare the strengths and weaknesses of direct and indirect evidence.
- Is it possible to have stronger and weaker types of direct evidence? Give some examples.

If we examine the first ionization energies of the period 2 elements, we observe a gradual increase, with some notable exceptions (see figure 1.1.6). Beryllium has a higher first ionization energy than boron. This suggests that Be has a greater stability than B. Similarly, nitrogen has a higher first ionization energy than oxygen. This pattern is repeated in periods 3, 4 and 5, although it is more difficult to observe in periods 4 and 5 due to the transition metals between groups 2 and 3. Generally speaking, it can be observed that group 2 elements have a greater stability than group 3 elements, and group 5 elements have a greater stability than group 6 elements.

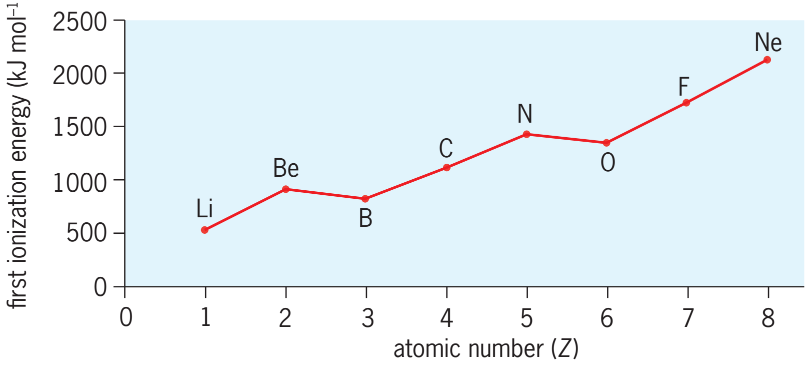

Figure 1.1.6 The first ionization energies of the period 2 elements.

This apparent stability could be expected to correspond, as with the noble gases, to a full electron shell; however, these atoms are still filling the second **main energy level**. This suggests the presence of **sub-levels** (**subshells**) within the main energy levels. The first sub-level in the 2nd energy level is filled with 2 electrons. The second sub-level appears to be filled by 3 electrons, with a third sub-level filled with a further 3 electrons. The other possibility, which we will discuss in section 1.2, is that the second sub-level gains some stability in becoming half-full, and its greatest stability is when it is completely full with 6 electrons in it.

Section 1.1 Exercises

1 Define the term *successive ionization energies*.

2 The list below gives the successive ionization energies of lithium.

$Li(g) \rightarrow Li^{+}(g) + e^{-}; I_1 = 513.3\ kJ\ mol^{-1}$

$Li^{+}(g) \rightarrow Li^{2+}(g) + e^{-}; I_2 = 7298\ kJ\ mol^{-1}$

$Li^{2+}(g) \rightarrow Li^{3+}(g) + e^{-}; I_3 = 11\,814.8\ kJ\ mol^{-1}$

Explain how these ionization energies can be used to determine the number of electrons in the valence shell of lithium.

3 The first six ionization energies (I_1 to I_6) of an element (in kJ mol^{-1}) are given below:

1060, 1890, 2905, 4950, 6270, 21 200

a State which group this element is in.

b Discuss whether this information is sufficient to state which period this element is in.

4 Locate the elements sodium, aluminium and sulfur on the periodic table.

  a State which group each of these elements is in.

  b State which of these three elements will have the highest second ionization energy and explain your answer.

5 Locate the elements magnesium and chlorine on the periodic table. State which of these two elements will have the higher third ionization energy and explain your answer.

6 Explain why the first ionization energy of magnesium is 900 kJ mol^{-1} while that of sodium is only 519 kJ mol^{-1}.

7 Explain why the first ionization energy of helium is greater than that of hydrogen, yet the first ionization energy of lithium is much less than that of helium.

8 The first ionization energies of the period 3 elements are as follows:

Element	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
First ionization energy (kJ mol^{-1})	494	736	577	786	1060	1000	1260	1520

Describe how the first ionization energies of these elements give evidence for the existence of energy levels and sub-levels in atoms.

1.2 ORBITALS, SUBSHELLS AND SHELLS

Although Bohr's model of the atom offered an explanation for the line spectrum of hydrogen (*Chemistry: For use with the IB Diploma Programme Standard Level*, chapter 1) it could only explain the line spectra of other atoms in a rather crude manner. In addition, Bohr's model of the atom could not explain the apparent existence of energetic sub-levels, as identified by a study of first ionization energies (see previous section).

The modern model of the atom is a consequence of the work of several scientists of the 1920s. The work of Louis de Broglie, a French physicist, followed on from that started by Albert Einstein and Max Planck. In 1924 de Broglie proposed that 'any moving particle or object had an associated wave'. Electrons had been found to exhibit **wave-like properties**, so an acceptable model of atomic structure needed to take this into account. Werner Heisenberg proposed that the dual nature of matter places a limitation on how precisely we can know the location of a subatomic particle such as an electron. This is known as the **Heisenberg uncertainty principle**.

In 1925 Wolfgang Pauli formulated a quantum mechanical principle that led to the understanding that no two electrons could have identical quantum numbers. The quantum numbers for an electron uniquely describe its position. This is known as the Pauli exclusion principle.

Erwin Schrödinger used these ideas in 1926 to generate a mathematical model to describe the behaviour of electrons in atoms. His model correctly predicted the energy levels of the electrons in all atoms. Schrödinger's model of the atom is known as **quantum mechanics** or wave mechanics.

Figure 1.2.1 Erwin Schrödinger, the Austrian physicist whose series of papers published in 1926 founded the science of quantum mechanics.

Orbitals

Quantum mechanics places the electrons in **orbitals**, not fixed orbits. This is because the path of an electron cannot be tracked accurately (the Heisenberg uncertainty principle). The electrons are like a cloud of negative charge within the orbital and the exact position of the electron cannot be stated with certainty.

> **An orbital is a region of space in which an electron or electrons may be found.**

CHEM COMPLEMENT

Why s, p, d and f?

The letters s, p, d and f are used to name atomic orbitals of elements in the periodic table. Theoretically there are further atomic orbitals named alphabetically as g, h …; however, there is no element that is currently known with electrons in a g or h orbital in the ground state.

The letters s, p, d and f appear to be rather random with no obvious reason for their relationship to the spherical s orbital, dumbbell-shaped p orbitals, and d and f orbitals of various shapes. History gives us the link to these names.

In the early 20th century, scientists were trying to understand the patterns of lines in the emission spectra of alkali metals. These lines were recorded on photographic film and they appeared with differing quality. In classifying these lines, scientists referred to them as **s**harp or **d**iffuse (meaning ‘fuzzy’). Other lines were also found on the emission spectrum of hydrogen—**p**rincipal lines. The **f**undamental lines were lines that only appeared on the spectrum of the alkali metal.

Scientists used these terms to give the letter names to atomic orbitals: s, sharp; p, principal; d, diffuse; f, fundamental.

Interactive Animation
Representations of methane

Schrödinger’s wave equation gives us knowledge of the **probability** of finding an electron in a given position at a given instant. This probability density or electron density can be plotted on a set of three-dimensional axes. In any electron shell, the lowest energy electrons are found in an **s orbital**. A graph of probability against radial distance from the nucleus for the lowest-energy electrons in an atom is shown in figure 1.2.2. The probability of finding the electron is greatest at a distance of 0.529 Å (0.529×10^{-10} m) from the nucleus, and then decreases dramatically until it is zero at a distance of 3 Å.

AS 12.1.5
Draw the shape of an s orbital and the shapes of the p_x, p_y and p_z orbitals. © IBO 2007

When this graph is extended to three dimensions, the spherical shape of the orbital can be recognized. This is seen in the electron-density plot for an s orbital (figure 1.2.3). The density of the dots represents the probability of finding the electron. The higher the density, the more likely it is that an electron will be found in that region of space.

The electron-density graph for the next lowest energy electrons also describes a sphere. Like the first orbital, this is also an s orbital. According to Bohr’s model of the atom, these electrons are in the second energy level, or shell, so this orbital can be named the 2s orbital, where 2 indicates the second energy level and s indicates the type of orbital. The lowest energy electrons in the third energy level also produce a spherical electron density graph. When the three spherical s orbitals are compared, those at higher energy levels have a greater radius at which the greatest probability of finding an electron occurs.

This leads to the 1s, 2s and 3s orbitals being represented as spheres of increasing radii.

Radial electron distribution

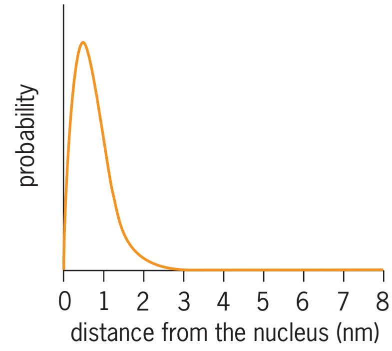

Figure 1.2.2 The radial probability graph for the lowest energy s orbital.

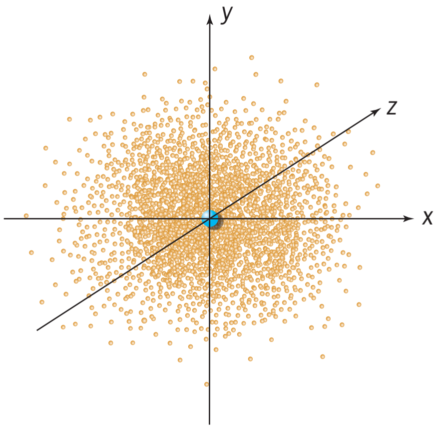

Figure 1.2.3 An electron-density plot shows the probability of finding an electron in a particular part of the space surrounding the nucleus.

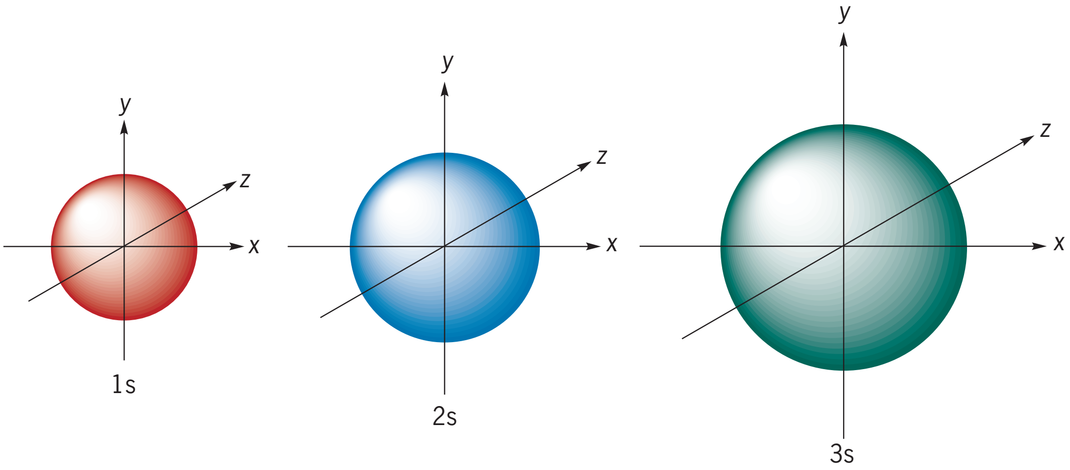

Figure 1.2.4 1s, 2s and 3s orbitals. The radii of the spheres correspond to a 90% probability of finding an electron within each sphere.

The electron density plots of the remaining electrons in the second energy level are very different from the spherical s orbitals. The electron-density plots for these orbitals take on a shape that is best described as a dumbbell. The dumbbell has two lobes and between the two lobes there is a **node** at which the probability of finding an electron is zero. This is not surprising, as the region between the two lobes contains the nucleus. The dumbbell-shaped orbitals are the p orbitals. The difference between the three p orbitals relates to the axis along which the orbital is aligned. This can be seen in figure 1.2.5 where a **p_x orbital** is aligned with the *x*-axis, a **p_y orbital** is aligned with the *y*-axis and a **p_z orbital** is aligned with the *z*-axis.

PRAC 1.1
Modelling orbitals

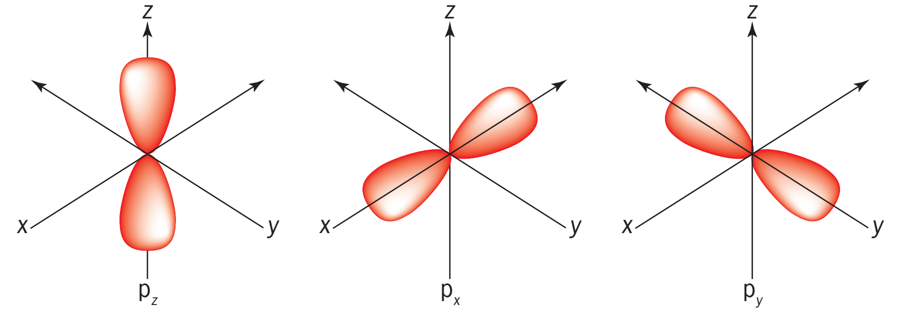

Figure 1.2.5 There are three different p orbitals, each of which is aligned with a different axis.

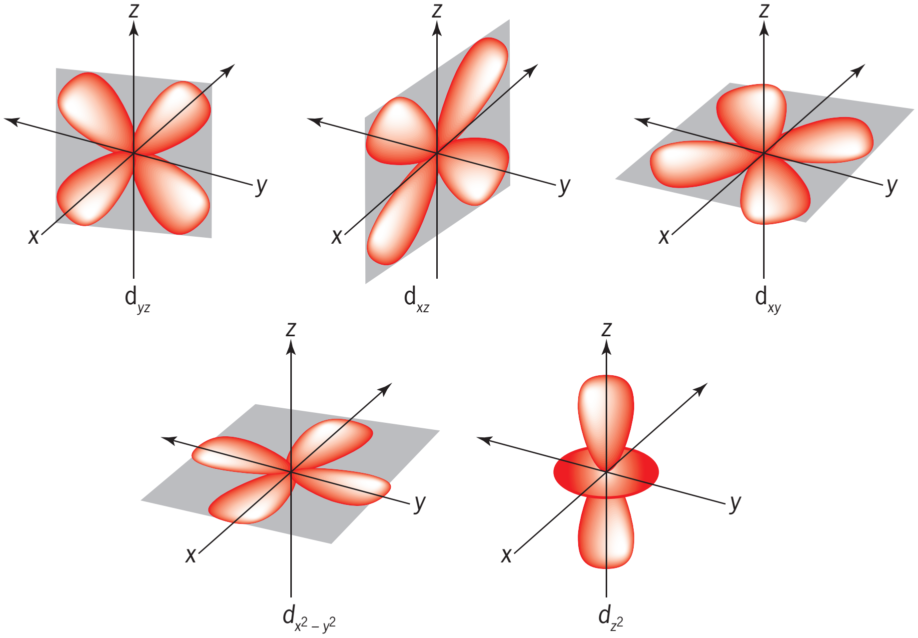

Figure 1.2.6 There are five different d orbitals, four of which are aligned in a plane defined by a pair of axes; the fifth is aligned along the *z*-axis.

AS 12.1.3
State the relative energies of s, p, d and f orbitals in a single energy level. © IBO 2007

The Bohr model of the atom described the increasing energy of electron shells as their distance from a nucleus increases. In quantum mechanics, an electron shell or energy level is a collection of orbitals with the same approximate energy. Electron shells of increasing energy are made up of increasingly larger numbers of orbitals. Within the energy level, the orbitals have increasing energy. The s orbitals have the lowest energy in the energy level, the p orbitals have the next highest energy, the d orbitals have the next highest and the f orbitals have the highest energy.

A group of orbitals with the same energy is called a subshell.

The number of orbitals that make up a subshell increases as the energy of the orbitals increases.

There is only one *s* orbital in an s subshell, there are three p orbitals in a p subshell, five d orbitals in a d subshell and seven f orbitals in an f subshell. Figure 1.2.7 shows the increasing energy of the subshells.

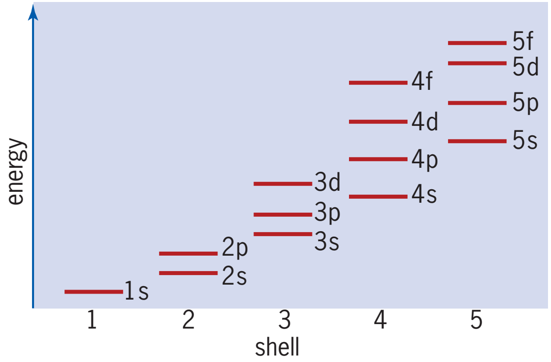

Figure 1.2.7 The energy of the subshells increases from s to p to d to f.

CHEM COMPLEMENT

Quantum numbers

In quantum mechanics, an electron is assigned a set of **quantum numbers** that describe its exact location. The principal quantum number, *n*, gives its main energy level or shell. Principal quantum numbers can have positive integral values such as 1, 2, 3, 4 etc. The second quantum number is called the angular momentum quantum number, *l*. It can have integral values from 0 to *n* – 1 for each value of *n*. This quantum number defines the shape of the orbital. The letters s, p, d and f correspond to values of the second quantum number, namely 0, 1, 2, and 3 respectively. The magnetic quantum number, m_l, can have integral values between –1 and l, including 0. This quantum number describes the orientation of the orbital in space.

TABLE 1.2.1 THE RELATIONSHIP BETWEEN THE QUANTUM NUMBERS *n*, *l* AND m_l

n	Possible values of *l*	Subshell	Possible values of m_l
1	0	1s	0
2	0	2s	0
	1	2p	–1, 0, 1
3	0	3s	0
	1	3p	–1, 0, 1
	2	3d	–2, –1, 0, 1, 2
4	0	4s	0
	1	4p	–1, 0, 1
	2	4d	–2, –1, 0, 1, 2
	3	4f	–3, –2, –1, 0, 1, 2, 3

In summary

The key descriptive features of the quantum mechanical model can be summarized as follows.

- Within an atom there are major energy levels or shells. Each energy level is assigned a number, starting at the nucleus and increasing outwards (1, 2, 3 …).
- The energy levels are further divided into subshells or sub-levels. These are assigned the letters s, p, d, f. Within an energy level, the energies of the subshells increase in the order s, p, d, f.
- Within subshells, electrons move in regions of space called orbitals.
- Subshells contain different numbers of orbitals. The s subshell contains 1 orbital, the p subshell 3 orbitals, the d subshell 5 orbitals and the f subshell 7 orbitals.

12.1.4
State the maximum number of orbitals in a given energy level.
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Orbital energy diagrams

TABLE 1.2.2 ENERGY LEVELS AND ORBITALS

Main energy level	Subshells in order of increasing energy	Orbitals in the subshell	Maximum number of orbitals in energy level
1	1s	1	1
2	2s	1	4
	2p	3	
3	3s	1	9
	3p	3	
	3d	5	
4	4s	1	16
	4p	3	
	4d	5	
	4f	7	

THEORY OF KNOWLEDGE

From JJ Thomson's discharge tube in the 1870s, through to Schrödinger's mathematical quantum mechanics model of today, advances made in understanding the structure of the atom have been significantly affected by advances in technology and mathematical modelling.

The science philospher Jacob Bronowski (1908–1974) once said:

> One of the aims of physical sciences has been to give an exact picture of the material world. One achievement in the twentieth century has been to prove that this aim is unattainable.

In the 1980s, long after Bronowski's death, science came one step closer to getting an exact picture of what atoms look like when Heinrich Rohrer from Switzerland and Gerd Binnig from Germany invented the scanning tunnelling microscope (STM). The STM scans the surface of an element and analyses the change in electric current over its surface. A three-dimensional image is then constructed using computer modelling, enabling a picture of individual atoms to be seen. The two scientists shared the 1986 Nobel Prize in Chemistry for their invention.

- Could there be knowledge about the structure of the atom that we don't know about yet because the technology or the mathematical models required do not exist?
- Do you think that the development of scientific knowledge is ultimately limited by advances in technology? What are the implications of this?
- What do you think Bronowski might have meant by his claim?
- The Nobel Prize is awarded every year in Chemistry to individuals or groups who have made a major contribution to the acquisition of knowledge that is of the 'greatest benefit to mankind'. Carry out some research on the scanning tunnelling microscope and find out why Rohrer and Binnig were such worthy recipients of the prize.

Section 1.2 Exercises

1 Draw a 1s orbital.

2 Compare a 1s and a 2s orbital.

3 Draw three sets of 3D axes.
  a On the first set of axes draw a p_x orbital.
  b On the second set of axes draw a p_y orbital.
  c On the third set of axes draw a p_z orbital.

4 Describe the spatial relationship between:
  a a p_x orbital and a p_y orbital
  b a p_x orbital and a p_z orbital

5 How does the energy of the 3p subshell compare with that of the:
  a 3s subshell?
  b 2p subshell?
  c 3d subshell?

6 Order the following subshells in order of increasing energy:
4s, 3d, 2p, 1s, 3p

7 **a** State the maximum number of orbitals in the 3rd energy level.
  b State the names of all the orbitals in the 3rd energy level.

8 **a** State the maximum number of orbitals in the 4th energy level.
  b State the name of the subshell with the highest energy in the 4th energy level.

1.3 WRITING ELECTRON CONFIGURATIONS

Knowledge of orbitals, subshells and their arrangement in the main energy levels enables us to write electron configurations for atoms and ions. Three principles govern the way in which electrons are placed in these orbitals, subshells and energy levels:

1. The **Aufbau** (or building-up) **principle** determines that electrons are placed into the lowest energy level available. This means that the subshell with the lowest energy is filled before the subshell with the next lowest energy can start to be filled.
2. The **Pauli exclusion principle** (proposed by the Austrian scientist Wolfgang Pauli) states that orbitals can hold 0, 1 or 2 electrons, but no more.
3. **Hund's rule** states that for orbitals of the same subshell, the lowest energy is attained when the number of electrons with the same spin (see Chem Complement) is maximized. Electrons will occupy orbitals singly until all orbitals of a subshell are half-full, then a second electron will be added to orbitals.

This information is summarized in table 1.3.1.

AS 12.1.6
Apply the Aufbau principle, Hund's rule and the Pauli exclusion principle to write electron configurations for atoms and ions up to $Z = 54$.
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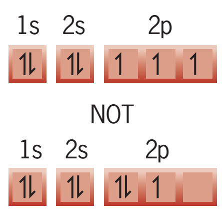


Figure 1.3.1 These orbital diagrams for nitrogen illustrate Hund's rule: 'Electrons will occupy orbitals singly until all orbitals of a subshell are half-full, then a second electron will be added to orbitals.'

QuickTime CW Video
Electron configurations

TABLE 1.3.1 MAXIMUM NUMBERS OF ELECTRONS IN ORBITALS

Main energy level	Subshells	Orbitals in the subshell	Maximum number of electrons in the subshell	Maximum number of electrons in energy level
1	1s	1	2	2
2	2s	1	2	8
	2p	3	6	
3	3s	1	2	18
	3p	3	6	
	3d	5	10	
4	4s	1	2	32
	4p	3	6	
	4d	5	10	
	4f	7	14	
n				$2n^2$

CHEM COMPLEMENT

Electron spin

Detailed study of the line spectra of many-electron atoms (i.e. atoms other than hydrogen) showed that each line was actually a pair of very closely spaced lines. This was explained by two Dutch physicists George Uhlenbeck and Samuel Goudsmit after an experiment by Otto Stern and Walther Gerlach in 1922 in which electrons were deflected in a magnetic field (see figure 1.3.2).

Electrons were postulated to have an intrinsic property, called **electron spin**, which causes each electron to behave as if it were spinning about an axis. The spinning charge generates a magnetic field whose direction depends on the direction of spin. This gives two possible values for a fourth quantum number,the spin magnetic quantum number, m_s.

This quantum number completes the description of an electron and allows the Pauli exclusion principle to be completely satisfied. No two electrons can have the same set of four quantum numbers. This results in the need for two electrons occupying the same orbital to have opposite spins. These are represented in **orbital diagrams** (see figure 1.3.1) by arrows pointing in opposite directions.

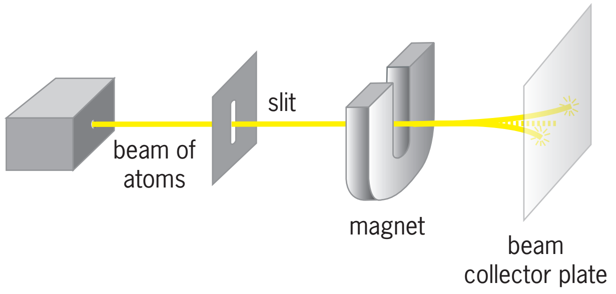


Figure 1.3.2 Atoms in which the electron spin quantum number of the unpaired electron is $+\frac{1}{2}$ are deflected in one direction and those in which it is $-\frac{1}{2}$ are deflected in the other.

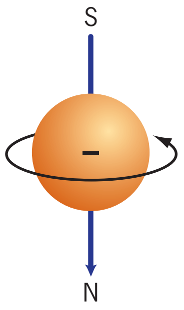


Figure 1.3.3 The direction in which an electron spins determines the direction of its magnetic field.

Note that an orbital containing electrons is said to be 'occupied'. Because they are regions of space, atomic orbitals exist whether they are occupied or not, but they are not included in an electron configuration unless they are occupied by one or more electrons.

Electron configurations can be represented in two ways: as an orbital diagram (electrons in boxes) or in a form that uses superscripts. An orbital diagram represents each orbital as a box and each electron as an ↿ or ⇂ arrow, so the positioning of the electrons in the individual orbitals can be shown clearly. Although orbital diagrams are a useful visual aid, they are not used routinely when a full electron configuration is required. The form of electron configuration with the superscripts is more commonly used to represent an atom or ions quickly. In this form the occupied subshells are written in order of increasing energy with the number of electrons in the subshell shown as a superscript.

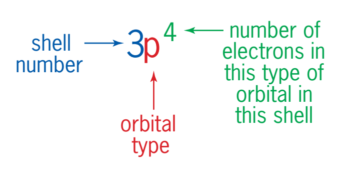


Figure 1.3.4 Electron configuration notation.

TABLE 1.3.2 **ELECTRON CONFIGURATIONS OF SEVERAL LIGHTER ELEMENTS**

Element	Total number of electrons	Orbital diagram 1s 2s 2p 3s	Full Electron configuration
Helium	2	[⥮] [ ] [ ][ ][ ] [ ]	$1s^2$
Lithium	3	[⥮] [↿] [ ][ ][ ] [ ]	$1s^2 2s^1$
Boron	5	[⥮] [⥮] [↿][ ][ ] [ ]	$1s^2 2s^2 2p^1$
Nitrogen	7	[⥮] [⥮] [↿][↿][↿] [ ]	$1s^2 2s^2 2p^3$
Fluorine	9	[⥮] [⥮] [⥮][⥮][↿] [ ]	$1s^2 2s^2 2p^5$
Sodium	11	[⥮] [⥮] [⥮][⥮][⥮] [↿]	$1s^2 2s^2 2p^6 3s^1$

CHEM COMPLEMENT

The f subshell

While the theoretical existence of the f subshell is of interest to those of us who wonder about what comes next, it is only the lanthanides and actinides that have electrons in the f subshell. (The lanthanides are named after element 57, lanthanum because they were thought to all have similar chemical properties to lanthanum.) However, the f orbitals are not occupied in the ground state until element 58 (cerium), so lanthanum is not officially part of the 'f-block'; however, on the basis of its chemical properties it is the first member of the lanthanides. Similarly, while actinium is the first member of the actinides, thorium is the first element with an electron in the 5f subshell. The f orbitals are buried deep beneath the valence shell and they rarely play an important role in chemical change or bonding. However, the orbital shapes can be useful in interpreting spectra and in understanding the structure of some complexes that involve the lanthanides and actinides.

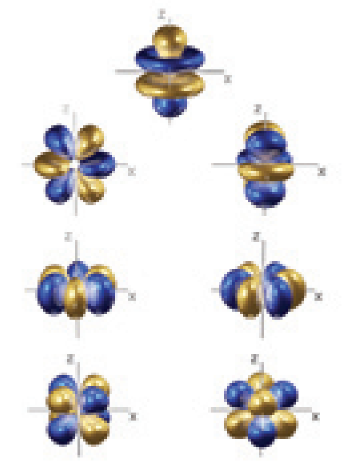


Figure 1.3.5 The shapes of the f orbitals are varied and unusual.

Electron configurations of elements with more than 18 electrons

In figure 1.2.7, the energies of all the subshells up to 5f are shown. Notice that the energy of the 4s subshell is *less* than that of the 3d subshell. This means that the 4s subshell fills *before* the 3d subshell. As a consequence of this filling order, the majority of the elements of the first transition series (V to Zn) have a full 4s subshell.

When the number of electrons becomes great (>20), even the shorter (subscript) form of writing the electron configuration becomes tedious. For note-taking purposes, a further shorthand form can be used in which the electron configuration of the previous noble gas is represented by the symbol for that element in square brackets (e.g. [Ar]) and is followed by the rest of the electron configuration for the element required. Using this shorthand the electron configuration of calcium would be [Ar]$4s^2$.

Note that this shorthand form should not be used when answering examination questions.

The periodic table can be used to great advantage in writing electron configurations. The periodic table can be divided up into blocks that reflect the subshell that is being filled.

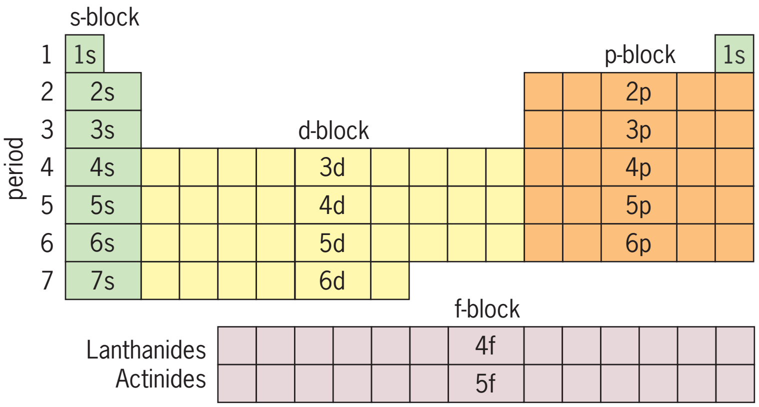


Figure 1.3.6 The periodic table can be divided up into blocks reflecting the subshell that is being filled.

Periodic table and order of filling

This view of the periodic table can be most useful in determining the electron configuration of any element. To determine an electron configuration:

Step 1: Locate the element on the periodic table.

Step 2: Determine the name of the block that the element is in (s, p, d, f)

Step 3: Count how many groups (vertical columns) from the left *of that block* the element is in.

Step 4: Determine which period the element is in by counting down from the first period, which consists of H and He.

Step 5: Fill all shells and subshells that have a lower energy than this subshell (see figure 1.2.7).

This information is used as follows:

1. The period in which the element is found gives you the last main energy level that is being filled. For example, if the element is in period 3, the last main energy level being filled is the 3rd energy level. Note the exceptions to this rule occur in the transition metals, where the 10 transition metals in period 4 are filling the 3d subshell and the 10 transition metals in period 5 are filling the 4d subshell.
2. The block in which the element is found gives you the subshell (s, p, d, or f) that is being filled. For example, if the element is in group 2 of the periodic table, it is in the s-block, so the s subshell is being filled.
3. The number of groups from the left gives you the number of electrons in that subshell e.g. an element in group 4 is 2 groups from the left-hand side of the p-block, so there are 2 electrons in the p subshell.

Worked example 1

State the full electron configuration of calcium.

Solution

Calcium ($Z = 20$) is in period 4, group 2, which is in the fourth column of the s-block of the periodic table.

This means that the last subshell being filled is the 4s subshell and this has 2 electrons in it.

The electron configuration of calcium is therefore $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$.

Worked example 2

State the electron configuration of tellurium.

Solution

Tellurium ($Z = 52$) is in period 5, group 6, which is in the fourth column of the p-block of the periodic table.

This means that the last subshell being filled is the 5p subshell and this has 4 electrons in it.

The electron configuration of tellurium is therefore $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$. In shorthand form this would be $[Kr]5s^2 4d^{10} 5p^4$. Remember that this shorthand form is not acceptable in examination answers, for which the full electron configuration must be written.

The periodic table can be used as a means by which to recall the relative energies of the subshells (see figure 1.2.7) and hence their order of filling. If you follow through the elements of the periodic table in atomic number order (hydrogen, helium, lithium, beryllium etc.) the order in which the blocks of the periodic table (see figure 1.3.6) are encountered gives the filling order of the subshells. Referring to figure 1.3.6, for elements 1 to 54, this would be:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p$$

where the 1s subshell has the lowest energy and the 5p subshell has the highest energy.

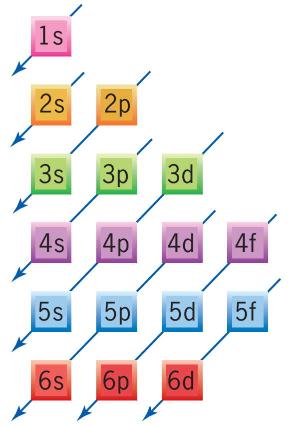


Figure 1.3.7 Another popular way of remembering the filling order of the subshells is to follow the arrows from top to bottom and right to left.

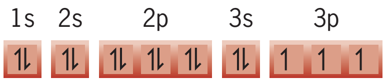


Figure 1.3.8 Orbital diagram for phosphorus.

When we were studying the first ionization energy of elements (see figure 1.1.5), it was clear that certain electron configurations possessed greater stability than others. In addition to the great stability offered by a full subshell, the peaks in figure 1.1.5 for N ($1s^2 2s^2 2p^3$) and P ($1s^2 2s^2 2p^6 3s^2 3p^3$) demonstrate a certain degree of stability in having a half-full subshell. The orbital diagrams for nitrogen (see table 1.3.2) and for phosphorus (see figure 1.3.8) show that these elements have one electron in each orbital of the p subshell.

When we consider the transition metals, the stability of a half-full d subshell is highly sought after. So much so, that when there are 4 electrons in a d subshell, 1 electron is 'borrowed' from the full *s* subshell of closest energy, so that the d subshell can be half-full. A similar situation arises when the d subshell is nearly full. When there are 9 electrons in a d subshell, 1 electron is 'borrowed' from the full s subshell to fill the d subshell. The resulting configurations for a small number of transition metals are shown in table 1.3.3.

TABLE 1.3.3 ELECTRON CONFIGURATIONS OF EXCEPTIONAL TRANSITION METALS

Element and atomic number (Z)		Orbital diagram and electron configuration										
		1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	
Chromium	24	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑	↑	☐ ☐ ☐	☐ ☐ ☐ ☐ ☐	☐	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	25	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑	↑↓	☐ ☐ ☐	☐ ☐ ☐ ☐ ☐	☐	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Copper	29	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	☐ ☐ ☐	☐ ☐ ☐ ☐ ☐	☐	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	30	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	☐ ☐ ☐	☐ ☐ ☐ ☐ ☐	☐	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$
Molybdenum	42	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑	↑	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^1$
Technetium	43	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑ ↑ ↑ ↑ ↑	↑↓	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$
Silver	47	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^1$
Cadmium	48	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2$

While this 'borrowing' of electrons from the full s subshell appears to break the Aufbau principle, it does result in an electron arrangement with a greater stability (lower energy), and so supports the Aufbau principle in this way.

Electron configurations of ions

An ion is formed when an atom loses or gains electrons. While an ion will have the same atomic number as an atom of the same element, it will have a different number of electrons and so will have a different electron configuration. The driving force behind formation of ions is the gaining of the same stability as the nearest noble gas, so ions of main group elements have the same electron configuration as the nearest noble gas.

WORKSHEET 1.2
Electron configurations

TABLE 1.3.4 ELECTRON CONFIGURATIONS OF IONS OF SOME MAIN GROUP ELEMENTS COMPARED TO THAT OF THE NEAREST NOBLE GAS

Element	Atomic number (Z)	Group	Symbol	Electron configuration
Neon	10	0	Ne	$1s^2 2s^2 2p^6$
Magnesium	12	2	Mg^{2+}	$1s^2 2s^2 2p^6$
Nitrogen	7	5	N^{3-}	$1s^2 2s^2 2p^6$
Argon	18	0	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	19	1	K^+	$1s^2 2s^2 2p^6 3s^2 3p^6$
Sulfur	16	6	S^{2-}	$1s^2 2s^2 2p^6 3s^2 3p^6$

Note in the table above that Ne, Mg^{2+} and N^{3-} ions have the same electron configuration, and Ar, K^+ and S^{2-} have the same electron configuration. These groups of ions are referred to as isoelectronic—having the same number of electrons.

Electron configurations of metal ions

Transition metal ions

The majority of the 3d transition metals have a full 4s subshell, although as discussed above, chromium and copper have only one electron in a 4s subshell. A full 4s subshell has a slightly higher energy than a partially filled 3d subshell (see chapter 3), so when a 3d transition metal loses electrons, the electrons are initially lost from the 4s subshell. If more than 2 electrons are lost, then the subsequent electrons are taken from the 3d subshell. Similarly, electrons are taken from the 5s subshell before the 4d subshell.

The electron configurations of some transition metal ions are shown below. These will be discussed in more detail in chapter 3.

TABLE 1.3.5 ELECTRON CONFIGURATIONS OF SOME TRANSITION METAL IONS

Element	Atomic number (Z)	Ion symbol	Number of electrons in the ion	Electron configuration
Iron	26	Fe^{2+}	24	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
Iron	26	Fe^{3+}	23	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
Vanadium	22	V^{2+}	20	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$
Chromium	24	Cr^{3+}	21	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
Copper	29	Cu^+	28	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
Copper	29	Cu^{2+}	27	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

Section 1.3 Exercises

1 State the maximum number of electrons that can be found in:

- **a** any p_x orbital
- **b** the first energy level
- **c** any d subshell
- **d** the second energy level
- **e** any s orbital

2 Draw an orbital diagram for each of the following elements.

- **a** Magnesium
- **b** Silicon
- **c** Chlorine

3 Describe how three electrons would be distributed in a p subshell that was previously empty.

4 Name the block of the periodic table in which each of the following elements is found.

- **a** Sodium
- **b** Carbon
- **c** Iron
- **d** Chlorine
- **e** Uranium
- **f** Silver

5 For each of the following elements, state the highest energy subshell that is being filled.

- **a** Oxygen
- **b** Chromium
- **c** Strontium
- **d** Aluminium
- **e** Arsenic
- **f** Rhodium

6 State the electron configuration of each of the following elements.

- **a** Nitrogen
- **b** Chlorine
- **c** Calcium
- **d** Nickel
- **e** Selenium
- **f** Tin

7 State the electron configuration of each of the following negative ions.

a F^- **b** Te^{2-} **c** P^{3-} **d** Br^-

8 State the electron configuration of each of the following positive ions.

a Mg^{2+} **b** Al^{3+} **c** Rb^+ **d** Zn^{2+}

Chapter 1 Summary

Terms and definitions

Aufbau principle When filling orbitals, electrons are placed into the lowest energy level available.

Electron configuration Notation showing main energy levels, subshells and number of electrons in the subshells that represents the electron arrangement in an atom.

Electron spin An intrinsic property of electrons that causes each electron to behave as if it were spinning about an axis. The spinning charge generates a magnetic field whose direction depends on the direction of spin.

First ionization energy The amount of energy required to remove one mole of electrons from one mole of atoms of an element in the gaseous state.

Heisenberg uncertainty principle There is a limitation on how precisely we can know the location of a subatomic particle such as an electron.

Hund's rule Electrons will occupy orbitals singly until all orbitals of a subshell are half-full, then a second electron will be added to the orbitals.

Main energy level A group of subshells with similar energies.

Nodes Positions on the electron density graph where the chance of finding the electron is zero.

Orbital A region of space in which an electron may be found.

Orbital diagram A diagrammatic representation of electron configuration showing electrons as ↿ and ⇂ arrows in boxes.

Pauli exclusion principle Orbitals can hold 0, 1 or 2 electrons, but no more.

Probability The chance of an event occurring.

p_x orbital A dumbbell-shaped orbital aligned with the x-axis.

p_y orbital A dumbbell-shaped orbital aligned with the y-axis.

p_z orbital A dumbbell-shaped orbital aligned with the z-axis.

Quantum mechanics A model of the atom based on quantum theory.

Quantum numbers A set of numbers that together uniquely describe the position of an electron.

Quantum theory Energy can be absorbed or emitted in 'packets' or quanta.

s orbital A spherical orbital that has the lowest energy in each main energy level.

Stability The amount of energy possessed by a particle. The greater the stability, the lower the energy of that particle and the lower the chance of it reacting to form another species.

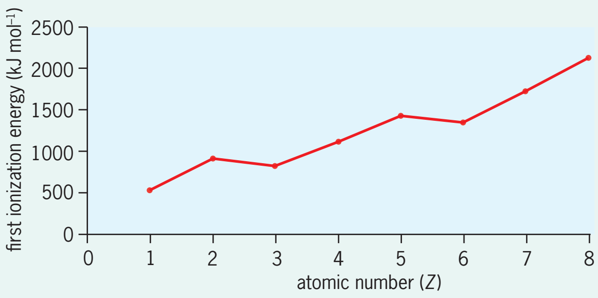
Subshell (sub-level) A group of orbitals all having the same energies.

Successive ionization energies The amounts of energy required to remove the electrons from one mole of an element in the gaseous state, one mole of electrons at a time.

Wave-like properties Physical properties that resemble those of waves rather than particles.

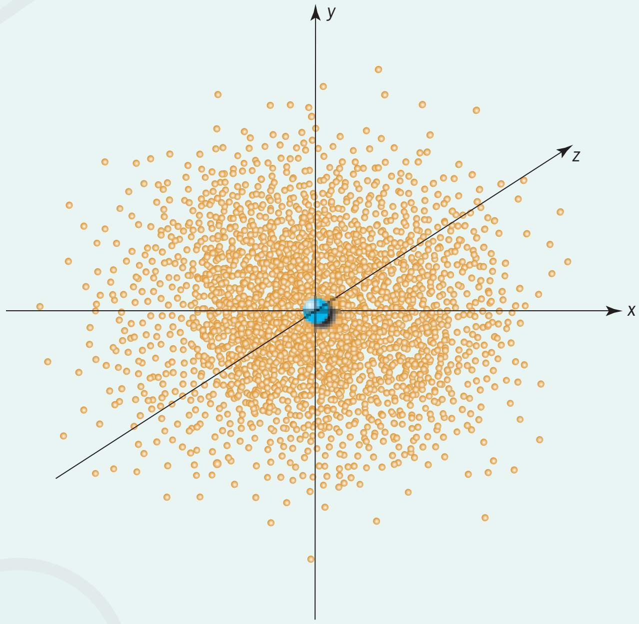
Concepts

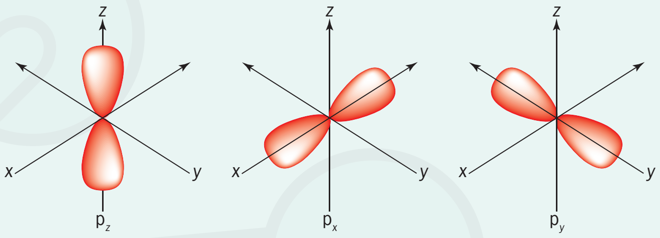
- A sharp increase from one successive ionization energy to the next indicates that the next electron is being removed from a full electron shell. In this way a graph of successive ionization energies relates to the electron configuration of an atom.
- The pattern of first ionization energies across a period gives evidence for the existence of main energy levels and sub-levels (subshells) in atoms due to peaks that correspond to full main energy levels and full sub-levels.



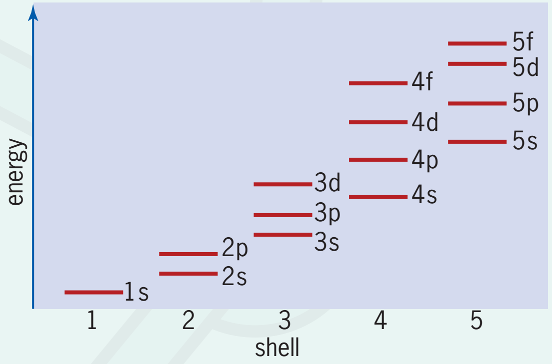
- A main energy level (shell) is made up of a number of subshells (sub-levels) of approximately the same energy. These subshells (sub-levels) are made up of a number of orbitals of the same energy.

- An s orbital is spherical and p orbitals are dumbbell shaped.





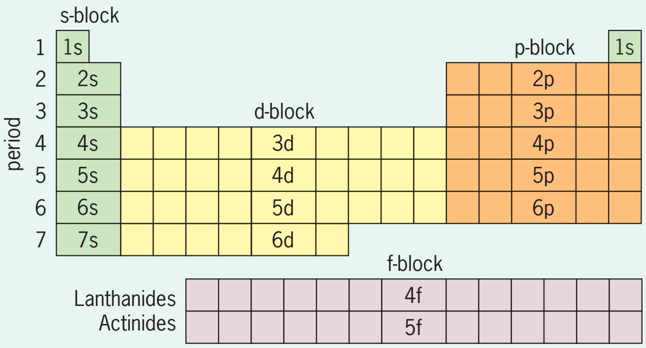
- In a main energy level the s subshell has the lowest energy, followed by the p subshell, the d subshell and finally the f subshell.



- Each subshell contains a fixed number of orbitals, and hence there is a maximum number of electrons that can be in the subshell.

Subshell (sub-level)	Number of orbitals	Maximum number of electrons
s	1	2
p	3	6
d	5	10
f	7	14

- The Aufbau principle determines that the electrons of an atom fill the energy levels in order of increasing energy.
- Hund's rule determines that when electrons fill a subshell, each orbital is half-filled before a second electron is added to any of the orbitals.
- The Pauli exclusion principle states that an orbital can contain 0, 1 or 2 electrons but no more.
- The above three rules are applied when an electron configuration is written.
- The position of an element in the periodic table can be used to determine electron configurations by determining the period (energy level), block (subshell) and position in the block (number of electrons in the subshell).



Chapter 1 Review questions

1 Define the term *first ionization energy*.

2 Explain how the first ionization energies of the elements in order of atomic number give evidence for the existence of energy levels and sub-levels (subshells).

3 Explain how successive ionization energies can be used to determine the group number of an atom.

4 Describe the pattern that you would expect for the successive ionization energies of sulfur.

5 State which period 2 element you would expect to have the highest 3rd ionization energy. Explain your answer.

6 Distinguish between an atomic orbital and an orbit.

7 Describe the:

- **a** shape
- **b** orientation on a set of three-dimensional axes
  - **i** of an s orbital
  - **ii** of a p_y orbital.

8 On a set of three-dimensional axes, sketch a p_z orbital and a p_x orbital.

9 List the following subshells in order of decreasing energy:

3p, 2s, 4s, 4p, 3d

10 State which of the following orbitals does not exist: 1p, 2s, 2d, 3d, 4f. Explain your answer.

11 State the total number of orbitals in the 4th main energy level and name four of them.

12 Compare a $2p_x$ orbital with a $2p_z$ orbital and describe the similarities and differences between them.

13 State the total number of:

- **a** p electrons in calcium
- **b** d electrons in zinc
- **c** s electrons in potassium.

14

- **a** Use orbital diagrams to show the six ways in which 2 electrons could be distributed in the p orbitals of the 2nd main energy level.
- **b** Consider the six diagrams you have drawn. Identify which of these agree with Hund's rule.

15 Draw orbital diagrams for atoms of the following elements.

- **a** Oxygen
- **b** Argon
- **c** Scandium
- **d** Gallium

16 For each of the following elements:

- **i** State the highest energy subshell that is being filled.
- **ii** State the number of electrons in that subshell.

- **a** Lithium
- **b** Fluorine
- **c** Paladium
- **d** Barium
- **e** Xenon
- **f** Germanium

17 State the electron configuration for each of the following elements.

- **a** Beryllium
- **b** Silicon
- **c** Iodine
- **d** Sodium
- **e** Niobium
- **f** Aluminium

18 State the electron configuration of each of the following negative ions.

- **a** Cl^-
- **b** S^{2-}
- **c** N^{3-}
- **d** Se^{2-}

19 State the electron configuration of each of the following positive ions.

- **a** Ba^{2+}
- **b** Ni^{2+}
- **c** K^+
- **d** B^{3+}

20 State the electron configuration of:

- **a** Cr
- **b** Cu
- **c** Ag
- **d** Mo

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Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 1 Test

Part A: Multiple-choice questions

1 What is the total number of electrons in p orbitals in an atom of iodine?

A 5

B 7

C 17

D 23

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2 A transition metal ion X^{2+} has the electronic configuration [Ar]$3d^9$. What is the atomic number of the element?

A 27

B 28

C 29

D 30

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3 Which statement is correct about electron orbitals and energy levels?

A Yttrium, Y ($Z = 39$) is the first element in the periodic table with an electron in a f sub-level.

B The maximum number of electrons in one d orbital is 10.

C The maximum number of electrons in the 4th main energy level is 18.

D In a main energy level, the sub-level with the highest energy is labeled f.

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4 Which is correct about the element tin (Sn) ($Z = 50$)?

	Number of main energy levels containing electrons	Number of electrons in highest main energy level
A	4	4
B	4	14
C	5	4
D	5	14

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5 Which equation represents the third ionization energy of an element M?

A $M^{+}(g) \rightarrow M^{4+}(g) + 3e^{-}$

B $M^{2+}(g) \rightarrow M^{3+}(g) + e^{-}$

C $M(g) \rightarrow M^{3+}(g) + 3e^{-}$

D $M^{3+}(g) \rightarrow M^{4+}(g) + e^{-}$

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6 In which of the following ground-state electron configurations are unpaired electrons present?

I $1s^2\ 2s^2\ 2p^2$

II $1s^2\ 2s^2\ 2p^3$

III $1s^2\ 2s^2\ 2p^4$

A II only

B I and II only

C II and III only

D I, II and III

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7 How many electrons are there in all the d orbitals in an atom of xenon?

A 10

B 18

C 20

D 36

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8 Which atom or ion has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$?

A Co

B Mn

C Co^{2+}

D Fe^{3+}

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9 A solid element, X, contains unpaired electrons in its atoms and forms an ionic chloride, XCl_2. Which electron configuration is possible for element X?

A [Ne]$3s^2$

B [Ar]$3d^2\ 4s^2$

C [He]$2s^2\ 2p^2$

D [Ne]$3s^2\ 3p^4$

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10 Values for the first ionization energies (IE) for five successive elements in the periodic table are given below. Based on these values, which statement is correct?

Element	K	L	M	N	O	P
IE / kJ mol^{-1}	1060	1000	1260	1520	418	?

A The outermost electron in element K is in a higher energy level than that in element L.

B Element M is probably a metal.

C Element N is probably a non-metal.

D Element P has a lower first ionization than element O.

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 Using the periodic table inside the cover of this coursebook, give the symbol(s) of:

a an ion with a double positive charge (2+) with an electronic configuration of [Ar]3d^5.

(1 mark)

b **two** elements with a ground state configuration of ns^2np^3.

(1 mark)

© IBO HL Paper 2 May 01 Q1a ii, iii

2 **a** State the full electron configuration for a bromide ion.

(1 mark)

b Write the symbol for the ion with a 2+ charge which has the electron configuration of $1s^22s^22p^6$.

(1 mark)

c Write the symbols for **three** other species, which also have the electron configuration of $1s^22s^22p^6$.

(2 marks)

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3 **a** **i** Explain why successive ionization energies of an element increase.

(1 mark)

ii Explain how successive ionization energies account for the existence of three main energy levels in the sodium atom.

(3 marks)

b State the formula of a stable ion formed from elemental vanadium. Identify which electrons are lost when the ion forms.

(2 marks)

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4 **a** Explain why the first ionization energy of magnesium is lower than that of fluorine.

(2 marks)

b Write an equation to represent the third ionization energy of magnesium. Explain why the third ionization energy of magnesium is higher than that of fluorine.

(3 marks)

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5 Outline why the first ionization energy of Al is lower than that of Mg in terms of electronic configuration.

(2 marks)

© IBO HL Paper 2 Nov 03 Q6 b(i)

Part C: Data-based question

Explain the difference in the two values of ionization energy for each of the following pairs:

a The 1st ionization energy of beryllium is 900 kJ mol^{-1} whereas the 2nd ionization energy of beryllium is 1757 kJ mol^{-1}.

(2 marks)

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b The 1st ionization energy of aluminium is 577 kJ mol^{-1} whereas the 1st ionization energy of magnesium is 736 kJ mol^{-1}.

(2 marks)

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c The successive ionization energies of germanium are shown in the following table:

	1st	2nd	3rd	4th	5th
Ionization energy / kJ mol^{-1}	760	1540	3300	4390	8950

i Identify the sub-level from which the electron is removed when the first ionization energy of germanium is measured.

(1 mark)

ii Write an equation, including state symbols, for the process occurring when measuring the second ionization energy of germanium.

(1 mark)

iii Explain why the difference between the 4th and 5th ionization energies is much greater than the difference between any two other successive values.

(2 marks)

Part D: Extended-response questions

1 **a** Describe how the first **four** ionization energies of aluminium vary. (You may wish to sketch a graph to illustrate your answer.)

(2 marks)

b State the electronic configurations of aluminium, boron and magnesium. Explain how the first ionization energy of aluminium compares with the first ionization energies of boron and magnesium.

(5 marks)

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2 The successive ionization energies for boron are given below in kJ mol^{-1}.

1st	2nd	3rd	4th	5th
799	2420	3660	25 000	32 800

a Explain the reason why there is a large increase between the third and fourth values.

(2 marks)

b Explain the reason why the increase between the first and second ionization energies is more than the increase between the second and third ionization energies.

(2 marks)

c State, with reasons, how the value for the second ionization energy of carbon would compare with that of the second ionization energy of boron.

(2 marks)

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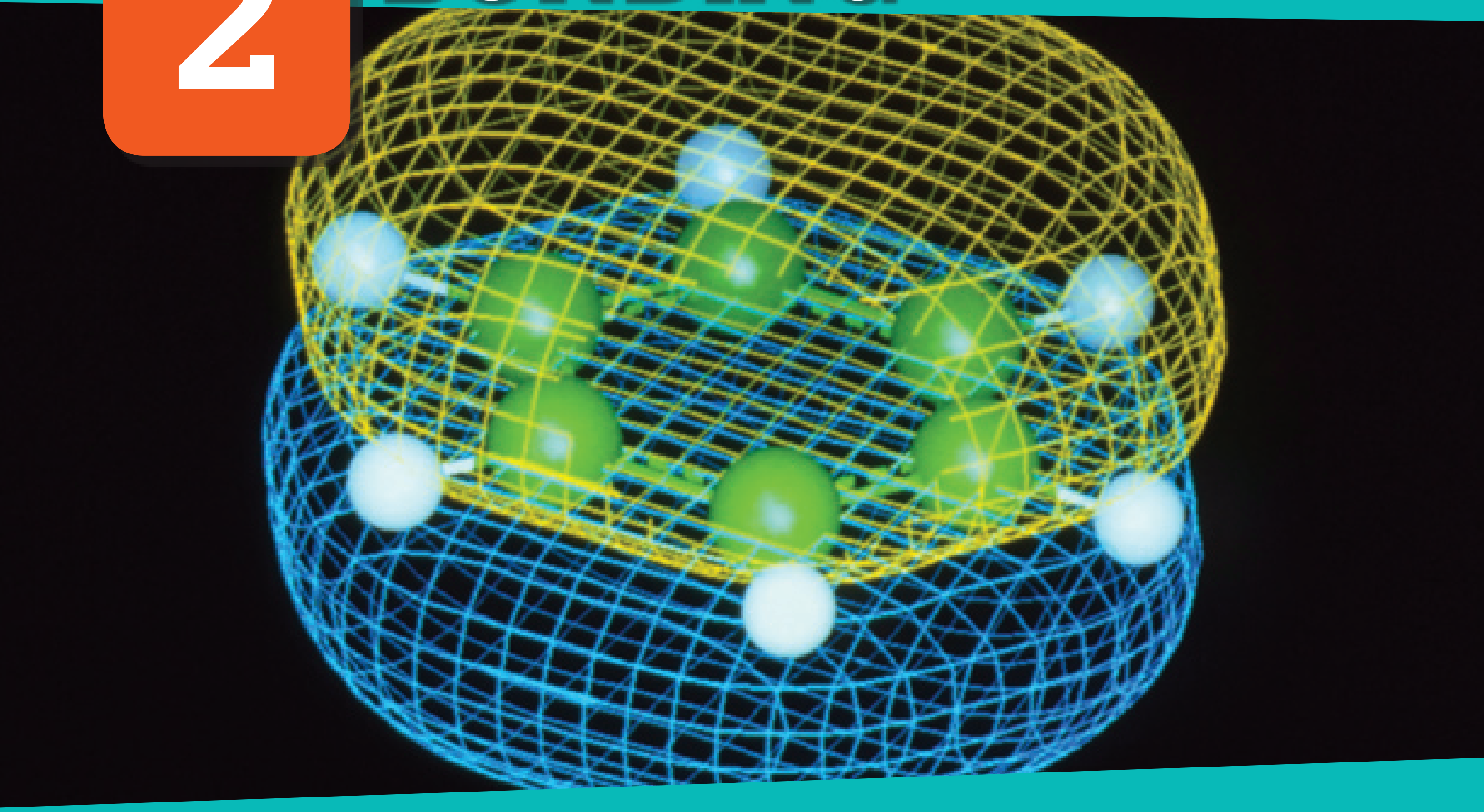
Total marks: 50

2 BONDING



Chapter overview

This chapter covers the IB Chemistry syllabus Topic 14: Bonding.

By the end of this chapter, you should be able to:

- use the VSEPR theory to predict and describe the shape and bond angles of molecules and ions with five and six pairs of bonding or non-bonding electrons
- describe sigma (σ) bonds in terms of the end to end overlapping of hybrid or atomic orbitals
- describe pi (π) bonds in terms of the side by side overlapping of p orbitals
- explain hybridization of atomic orbitals as the mixing of atomic orbitals to form new orbitals that are suitable for bonding
- compare and explain the relationships between Lewis structures, molecular shapes and types of hybridization
- describe the structures of selected molecules and ions in terms of delocalization of π electrons.

IBO Assessment statements 14.1.1 to 14.3.1

The shape of a molecule is important in determining how it interacts with other molecules around it. The shape may govern whether the molecule is polar or non-polar and hence how strongly it is attracted to other molecules by intermolecular forces.

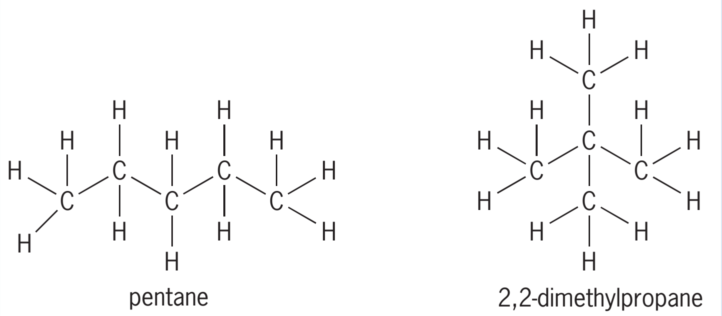


Figure 2.0.1 The higher boiling point of pentane in comparison to its isomer 2,2-dimethylpropane can be attributed to the difference in their shapes.

When two non-polar hydrocarbons of equal molecular mass are compared, the ease with which the molecules can pack together in the liquid state will be governed by their shapes, and will cause a difference in their boiling points—the more linear the shape of the molecule, the more easily the molecules will pack together, the stronger the van der Waals' forces between them and the higher the boiling point of the hydrocarbon. Two isomers of pentane, C_5H_{12}, illustrate this point clearly. The boiling point of pentane, the straight-chain isomer, is 36.1°C while the boiling point of its isomer 2,2-dimethylpropane, a much more compact molecule, is only 9.5°C.

VSEPR theory

You will recall from your study of the shapes of molecules (*Chemistry: For use with the IB Diploma Programme Standard Level,* chapter 2,) that the repulsion between pairs of bonding electrons and non-bonding electrons determines the shape of a molecule. These pairs of electrons can be referred to as **negative charge centres**. A bonding electron pair is attracted by the nuclei of both bonding atoms. In comparison, a non-bonding electron pair is only attracted to one nucleus, so it experiences less nuclear attraction. Its negative charge centre spreads out more than does that of a bonding pair of electrons. As a result, the non-bonding pairs of electrons exert greater repulsive forces on adjacent pairs of electrons, so the repulsion between a non-bonding pair of electrons and a bonding pair of electrons is greater than that between two pairs of bonding electrons. An adjacent non-bonding pair of electrons will have the effect of compressing the bond angle.

Order of repulsion:
non-bonding–non-bonding > non-bonding–bonding > bonding–bonding

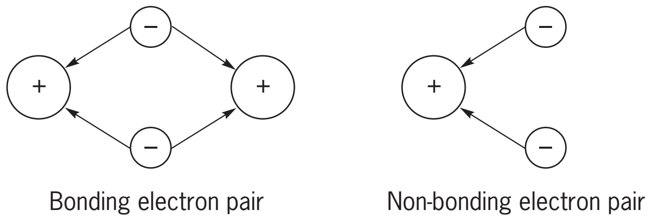


Figure 2.0.2 A bonding electron pair is attracted by the nuclei of both bonding atoms, while a non-bonding electron pair is only attracted to one nucleus.

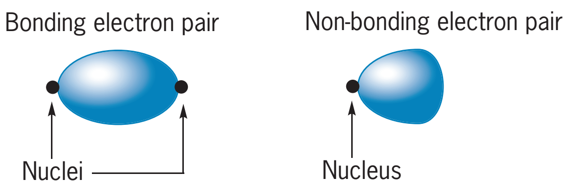


Figure 2.0.3 A non-bonding electron pair spreads out more in space than does a bonding electron pair.

Double and triple bonds (multiple bonds) each constitute one negative charge centre. Like a non-bonding electron pair, the negative charge centre of a multiple bond is larger than that of a single bond and exerts greater repulsive force on adjacent negative charge centres.

The basis of VSEPR theory is that the best arrangement of a given number of negative charge centres is the one that minimizes the repulsions between them. The shapes of different molecules or ions depend on the number of negative charge centres (electron domains) around the central atom.

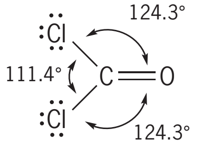


Figure 2.0.4 In this Lewis structure of Cl_2CO, the electrons of the C=O double bond exert a greater repulsive force than do the electrons in the C–Cl single bonds, so the O–C–Cl bond angle is 124.3° rather than 120° as found in trigonal planar molecules such as BF_3.

2.1 SHAPES OF MOLECULES AND IONS

The shapes and bond angles of molecules and ions with 2, 3 and 4 negative charge centres were discussed as part of the Standard Level course. In this chapter we will discuss the shapes and bond angles of molecules and ions with 5 and 6 negative charge centres.

In order to accommodate more than 4 pairs of electrons in the valence shell of an atom, the **octet rule** is broken. This 'expansion' of the valence shell is found to only occur for atoms in the 3rd period and beyond. It seems that the presence of an empty d orbital in the valence shell allows the extra electrons to be accommodated. In addition, the size of the central atom in the molecule is a factor. The larger the central atom, the larger the number of atoms that can surround it. The size of the surrounding atoms is also important. An expanded valence shell occurs most frequently when the surrounding atoms are small and highly electronegative, such as fluorine, oxygen and chlorine.

Five negative charge centres

AS 14.1.1
Predict the shape and bond angles for species with five and six negative charge centres using the VSEPR theory. ©IBO 2007

You will recall that in a Lewis structure, valence electrons are represented by dots or crosses. As a covalent bond consists of a pair of bonding electrons shared between two atoms, a dot and a cross between the atoms represent a bond, while pairs of dots or crosses represent non-bonding pairs of electrons.

As with simpler molecules, the first step in determining the shape of a molecule with five or more negative charge centres is to find out how many electrons are in the valence shell of the central atom. Next you should use the formula of the molecule to determine how many bonds the central atom forms with other atoms. The difference between these two numbers will give you the number of non-bonding electrons around the central atom. These non-bonding electrons can be paired up as non-bonding electron pairs or negative charge centres. The combination of bonding electron pairs and non-bonding electron pairs leads to the shape of the molecule (see table 2.1.1).

De
DEMO 2.1
Modelling five and six negative charge centres

When five atoms are bonded to a central atom, according to VSEPR theory, the pairs of bonding electrons (negative charge centres) will move as far apart as possible, in order to minimize the repulsions between them. The shape that the molecule takes on is called a **trigonal bipyramid**. This shape can be thought of as two trigonal pyramids fused together at their bases.

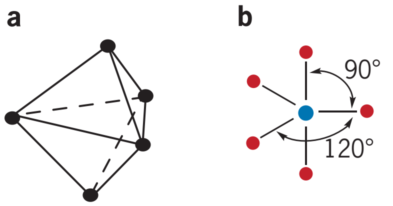


Figure 2.1.1 (a) A trigonal bipyramid has six faces and five vertices. (b) When five atoms are bonded to a central atom, the shape of the molecule is called a trigonal bipyramid.

There are three atoms in a plane forming an equilateral triangle around the middle of the molecule (the **equatorial positions**), one atom at the top and one atom at the bottom of the molecule (**axial positions**). The plane of the equatorial atoms is at right angles to that of the axial atoms.

Example 1: PCl_5

Phosphorus pentachloride (phosphorus(V) chloride) is a molecule in which a phosphorus atom has formed covalent bonds with five chlorine atoms. This results in the phosphorus atom having 10 electrons in its valence shell (an expanded valence shell). The shape of the molecule is described as trigonal bipyramidal and the molecule is non-polar. The bond angle between the equatorial atoms and the central phosphorus atom is 120°. This is consistent with the equilateral triangle formed by the three chlorine atoms in that position. The bond angle between an equatorial chlorine atom and an axial chlorine atom will be 90°.

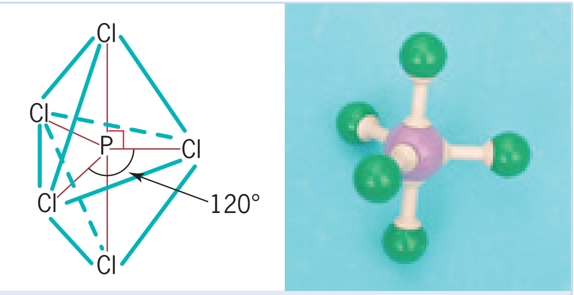


Figure 2.1.2 Phosphorus pentachloride, PCl_5, has a trigonal bipyramidal shape.

There are other molecules with five negative charge centres around them; however, phosphorus, being in group 5, is the only member of period 3 that bonds with five atoms and has no pairs of non-bonding electrons. The other molecules have combinations of bonding and non-bonding pairs of electrons, so with the greater electrostatic repulsion of the non-bonding charge centres and the smaller numbers of atoms bonded to the central atom, a range of shapes is assumed.

Example 2: ClF_3

Chlorine trifluoride is a very reactive, poisonous and corrosive gas. Chlorine has seven electrons in its valence shell and the formula tells us that three bonds are formed with fluorine. This leaves four non-bonding electrons (two pairs) in the valence shell. Consequently there are five negative charge centres around this chlorine atom—-three bonding and two non-bonding. The non-bonding pairs of electrons take up equatorial positions around the chlorine to minimize the electrostatic repulsions in the molecule. The angle between the equatorial fluorine and the axial fluorine atoms is slightly less than 90° (87.5°) due to the repulsive forces exerted by the non-bonding electrons. The shape of this molecule is commonly referred to as 'T-shaped'.

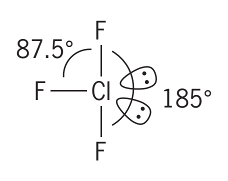
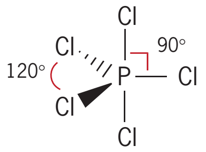
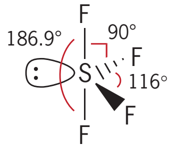
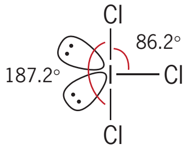
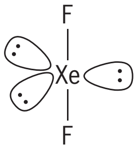


Figure 2.1.3 Chlorine trifluoride is a 'T-shaped' molecule.

In table 2.1.1 a range of shapes for molecules with five negative charge centres is shown. Notice the effect of the non-bonding electrons on the shapes (in particular the angle between axial atoms) of these molecules.

TABLE 2.1.1 SUMMARY OF MOLECULES WITH FIVE NEGATIVE CHARGE CENTRES AROUND THE CENTRAL ATOM

Number of bonding pairs on the central atom	Number of non-bonding pairs on the central atom	Example	Shape of molecule	Representation of the shape
5	0	PCl_5	Trigonal bipyramid	
4	1	SF_4	Seesaw or 'sawhorse'	
3	2	ICl_3	T-shaped	
2	3	XeF_2	Linear	

Six negative charge centres

When there are six negative charge centres around a central atom they will move as far apart as possible, according to VSEPR theory, in order to minimize the repulsions between them. If 6 atoms are bonded to the central atom, all six negative charge centres are bonding electron pairs and the shape that the molecule takes on is called an **octahedron**. This name comes from the solid shape formed when the vertices are joined. An octahedron has eight faces and six vertices. This shape can be thought of as two square pyramids fused together at their bases, and so can be described as **square bipyramidal**.

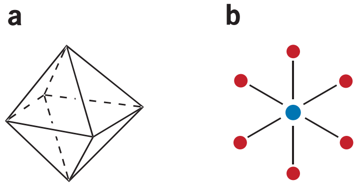


Figure 2.1.4 (a) An octahedron has eight faces and six vertices. (b) When six atoms are bonded to a central atom the molecule is octahedral.

In an **octahedral** molecule four atoms in a plane form a square around the middle of the molecule (the **equatorial positions**) and there is one atom at the top and one atom at the bottom of the molecule (**axial positions**). The plane of the equatorial atoms is at right angles to that of the axial atoms.

Example 3: SF_6

Sulfur hexafluoride (sulfur(VI) fluoride) is a molecule in which a sulfur atom has formed covalent bonds with six chlorine atoms. This results in the sulfur atom having 12 electrons in its valence shell (another example of an expanded valence shell). The shape of the molecule is described as octahedral or square bipyramidal and the molecule is non-polar. The bond angle between the equatorial atoms and the central sulfur atom (F–S–F) is 90°. This is consistent with the square formed by the four fluorine atoms in that position. The bond angle between an equatorial fluorine atom and an axial fluorine atom will be 90°.

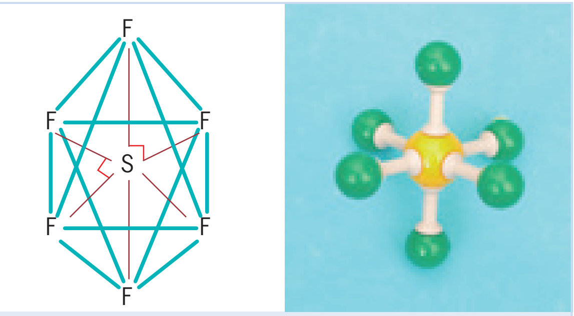


Figure 2.1.5 Sulfur hexafluoride, SF_6, has an octahedral shape.

Example 4: PF_6^-

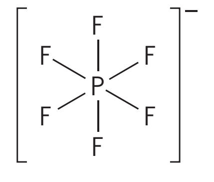


Figure 2.1.6 The phosphorus hexafluoride ion, PF_6^-, has an octahedral shape.

The phosphorus hexafluoride ion, PF_6^-, is a Lewis base that is formed when PF_5 reacts with XeF_2. While its chemistry is unusual, its shape is the same as that of sulfur hexafluoride—octahedral, or square bipyramidal. This molecule is an anion (negative ion) because in addition to the five fluorine atoms that would normally covalently bond with a phosphorus atom, an extra fluoride ion, F^-, has bonded in a dative covalent (coordinate) bond with the phosphorus atom. In PF_6^-, the phosphorus atom has 12 electrons in its valence shell.

There are other molecules with six negative charge centres around them; however, sulfur, being in group 6, is the only member of period 3 that bonds with six atoms to form a neutral molecule and has no non-bonding pairs of electrons. The other molecules have combinations of bonding and non-bonding pairs of electrons, so with the greater electrostatic repulsion of the non-bonding charge centres and the smaller numbers of atoms bonded to the central atom, a number of different shapes is assumed.

Example 5: XeF_4

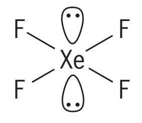


Figure 2.1.7 Xenon tetrafluoride, XeF_4, is a square planar molecule.

Under conditions of high voltage and with the very electronegative element fluorine, xenon will react to form xenon tetrafluoride, XeF_4. Xenon has 8 electrons in its valence shell. According to the formula, four bonds are formed, so there are four non-bonding electrons (two non-bonding pairs). These non-bonding pairs take up the axial positions in the octahedral arrangement of negative charge centres to minimize the electrostatic repulsions in the molecule. As a result, the XeF_4 molecule takes on a **square planar** shape in which the F–Xe–F bond angle is 90°. The XeF_4 molecule would be non-polar. Notice that there are 12 electrons in the valence shell of the xenon atom. The octet rule is certainly broken in this case!

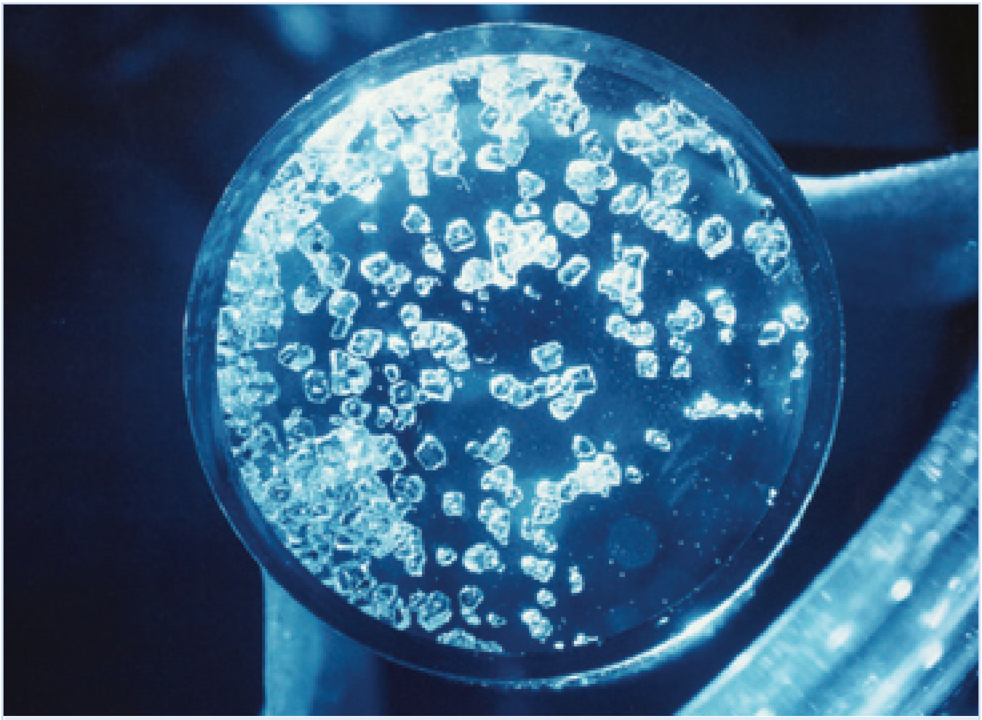
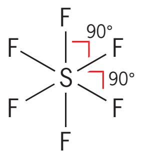
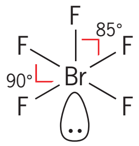
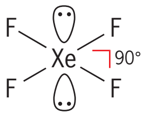


Figure 2.1.8 When xenon tetrafluoride is isolated, it forms colourless, roughly cubic crystals.

Table 2.1.2 summarizes the shapes that can be taken on by molecules with six negative charge centres. Notice that in the case of square pyramidal molecules, the one non-bonding pair of electrons repels the square plane upwards to give an angle that is less than 90° with the atom at the 'top' of the pyramid.

TABLE 2.1.2 SUMMARY OF MOLECULES WITH SIX NEGATIVE CHARGE CENTRES AROUND THE CENTRAL ATOM

Number of bonding pairs on the central atom	Number of non-bonding pairs on the central atom	Example	Shape of molecule	Representation of the shape
6	0	SF_6^-, PF_6^-	Octahedral or square bipyramidal	
5	1	BrF_5	Square pyramidal	
4	2	XeF_4	Square planar	

WORKSHEET 2.1
VSEPR for five and six negative charge centres

Interactive Animation
VSEPR: Basic molecular configurations table

Section 2.1 Exercises

1 The valence-shell electron pair repulsion (VSEPR) theory is used to predict the shape of molecules. Explain how these predictions are made.

2 Outline the meaning of the term *negative charge centre*.

3 Draw and name the four shapes that can be taken on by molecules with five negative charge centres around the central atom.

4 Explain how the shape in which six atoms are arranged around a central atom can be called 'octahedral'.

5 Describe how the repulsion between a non-bonding pair of electrons and a bonding pair of electrons compares with that between two bonding pairs of electrons.

6 Describe how the repulsion between a non-bonding pair of electrons and a bonding pair of electrons compares with that between two non-bonding pairs of electrons.

7 Draw and name the shape of a molecule with four bonding pairs of electrons and two non-bonding pairs of electrons around the central atom.

8 Draw each of the following molecules and state their shape according to VSEPR theory.

a PF_5

b IF_5

c XeF_4

d SF_4

2.2 HYBRIDIZATION

In Lewis theory, a covalent bond is a shared pair of electrons. This suggests that there is a region of electron density between two atoms as a result of the electron pair being shared. Atomic orbital theory (see chapter 1, section 1.2) suggests that electrons exist in atomic orbitals that are regions of space surrounding the nucleus of an atom. Each atomic orbital can hold no more than two electrons. If covalent bonding is approached from the perspective of quantum mechanics, the question 'How can we use atomic orbitals to explain bonding and to account for the shapes of molecules?' can be asked. This leads to a model of chemical bonding called **valence-bond theory**.

Overlapping orbitals

In valence-bond theory, a region of electron density between two atoms is explained in terms of the overlap of two atomic orbitals. Two orbitals from different atoms, each containing one unpaired electron, can merge in the region of space between the two atoms. This overlapping of two orbitals creates a bonding orbital between the two atoms.

When two p orbitals overlap in the same axis, or an s orbital and a p orbital or even two s orbitals overlap, the bond formed is called a σ **(sigma) bond**.

AS 14.2.1
Describe σ and π bonds.
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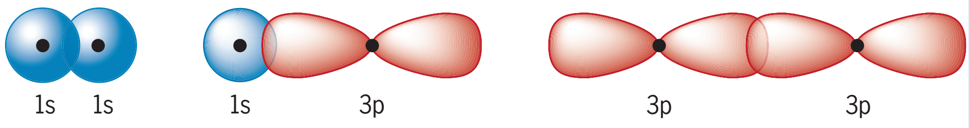


Figure 2.2.1 (a) Overlap of two 1s orbitals to form a σ bond between two H atoms, (b) overlap of a 1s orbital and a 3p orbital to form a σ bond between an H atom and a Cl atom and (c) overlap of two 3p orbitals to form a σ bond between two Cl atoms.

This overlapping of orbitals explains the difference in bond length between two single bonds, such as an F–F bond and a Cl–Cl bond. The two orbitals overlapping in the case of the F–F bond are both 2p orbitals, whereas in the case of the Cl–Cl bond, the overlapping orbitals are both 3p orbitals. The 3p orbitals are larger than the 2p orbitals, so when two 3p orbitals overlap, they do so at a greater distance from the nucleus than do two 2p orbitals. This causes the bond length in Cl_2 to be greater than that in F_2.

You will recall from chapter 1 that the three p orbitals are at right angles to each other. When two p_x orbitals are overlapping in a σ bond, the other two p orbitals, p_y and p_z are not overlapping.

When two atoms come close enough together, the p_y and/or the p_z orbitals are able to overlap in a sideways fashion. This sideways overlapping of two orbitals is called a π **(pi) bond**. In a π bond the overlapping is not as great as in a σ bond, so a π bond is not as strong as a σ bond.

π bonds occur most commonly when a multiple bond (a double or a triple bond) is formed. A double bond is formed by one σ bond and one π bond. Since a π bond is not as strong as a σ bond, a double bond is less than twice as strong as a single covalent bond between the same two elements. A triple bond is formed by one σ bond and two π bonds and is less than three times as strong as a single bond.

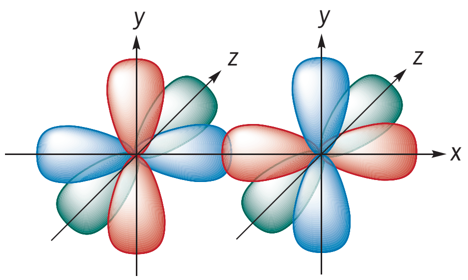


Figure 2.2.2 When the p_x orbitals are overlapping end to end in a σ bond, the p_y and p_z orbitals are not.

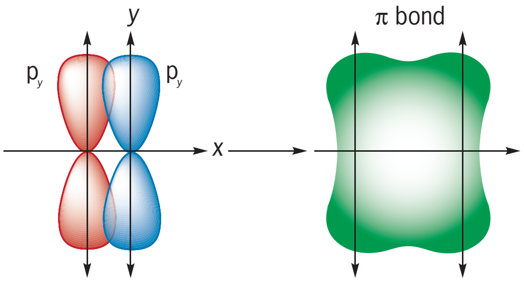


Figure 2.2.3 When p_y and p_z orbitals are brought close enough together they overlap sideways to form a π bond.

Hybrid orbitals

Bond lengths can tell us much about the equality (or otherwise) of covalent bonds between atoms. When the bond lengths of the four C–H bonds in methane, CH_4, are measured, they are all found to be equal. This suggests that they are identical in nature. To explain these bonds using the concept of overlapping atomic orbitals, we need to consider the electronic configuration of the atoms involved.

The electronic configuration of carbon is $1s^2 2s^2 2p^2$ and that of hydrogen is $1s^1$. An orbital that overlaps with another must have only one electron in it, so that the new overlapping (bonding) orbital has no more than 2 electrons in it. With this in mind, the valence shell configuration of carbon, $2s^2 2p^2$, causes problems. There are only 2 orbitals with just one electron in them. The 2s orbital is full and the third 2p orbital has no electrons in it at all.

QuickTime CW Video
Hybridization

This can be shown using an **orbital diagram** (electrons in boxes).

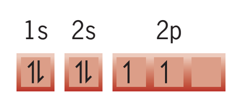


Figure 2.2.4 The orbital diagram for carbon suggests that there are only two orbitals that could be involved in bonding.

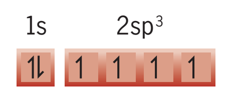


Figure 2.2.5 In the orbital diagram for a hybridized carbon atom, four orbitals could be involved in bonding.

If the four bonds that carbon is commonly observed to make are to exist, there must be four unpaired electrons in the valence shell. This is made possible if the atomic orbitals in the valence shell are assumed to mix together to make **hybrid orbitals** (figure 2.2.5). The shape of a hybrid orbital is different from that of the two orbitals from which it is formed, but the total number of orbitals in the valence shell remains the same.

AS 14.2.2
Explain hybridization in terms of the mixing of atomic orbitals to form new orbitals for bonding.
© IBO 2007

Note that there is no energy change involved in forming hybrid orbitals; that is, the total energy is the same before and after **hybridization** has occurred.

> **The process of mixing atomic orbitals as atoms approach each other is called hybridization.**

DEMO 2.2
Modelling hybridization

sp^3 hybridization

The case of carbon's four equal bonds can be explained by hybridization. The four orbitals in the valence shell of carbon, 2s, $2p_x$, $2p_y$ and $2p_z$, are mixed together. Whenever we mix a certain number of atomic orbitals, the same number of hybrid orbitals is formed. Hence, when the four valence shell orbitals of carbon are mixed together, we get four sp^3 hybrid orbitals.

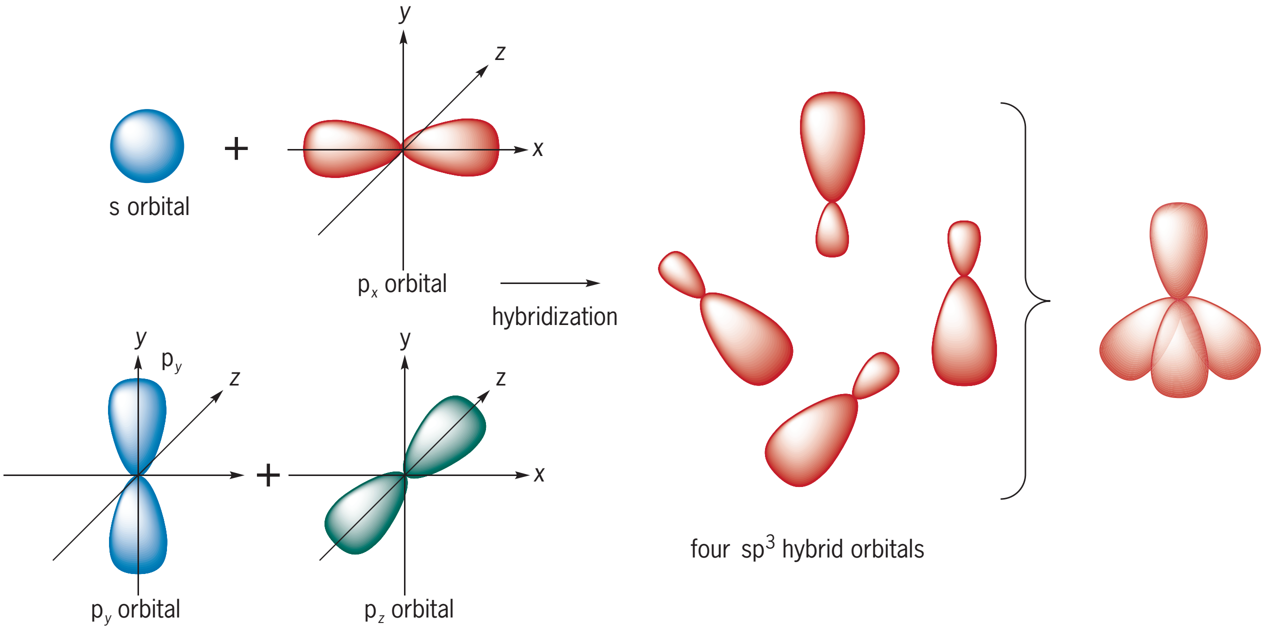


Figure 2.2.6 One s orbital and three p orbitals mix to form four sp^3 hybrid orbitals.

The shape of an sp^3 hybrid orbital is not the same as either the s orbital or the p orbital. Like p orbitals it has two lobes, but, unlike p orbitals, one lobe is much bigger than the other. When put together, the four lobes of the sp^3 orbitals take up a tetrahedral shape in space. This shape allows the electron pairs to be as far apart as possible, so as to minimize electrostatic repulsion. The H–C–H bond angle is 109.5°. In this manner the hybridization of atomic orbitals agrees with the requirements of VSEPR theory. Each orbital is equal in size, hence allowing the four bonds to be equal in length and strength when they overlap with the orbital of another atom.

Whenever there are four negative charge centres around a central atom, the hybridization of that central atom must be sp^3. This is illustrated by the following examples.

AS 14.2.3
Identify and explain the relationships between Lewis structures, molecular shapes and types of hybridization (sp, sp^2 and sp^3). © IBO 2007

Interactive CW Animation
sp hybridization

Example 1: Methane, CH_4

A molecule of methane, CH_4, is formed when each of the four sp^3 hybrid orbitals of carbon overlap in σ bonds with the s orbitals of four hydrogen atoms. The shape of the molecule is tetrahedral.

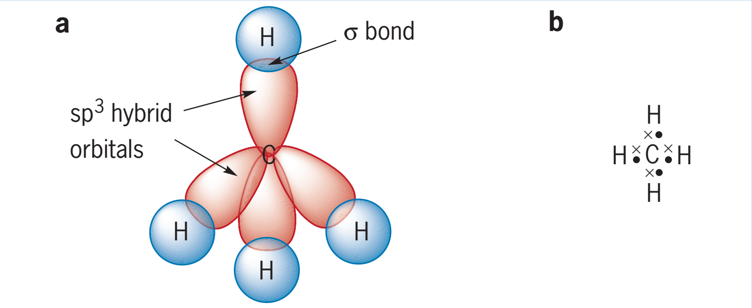


Figure 2.2.7 (a) The σ bonding between sp^3 hybrid orbitals of carbon and s orbitals of hydrogen in methane. (b) The Lewis structure of methane.

Example 2: Ethane, C_2H_6

Each of the two carbon atoms in ethane exhibits sp^3 hybridization. Each carbon forms four bonds—three to hydrogen atoms and one to the other carbon atom. There is a tetrahedral arrangement of bonding electron pairs around each carbon.

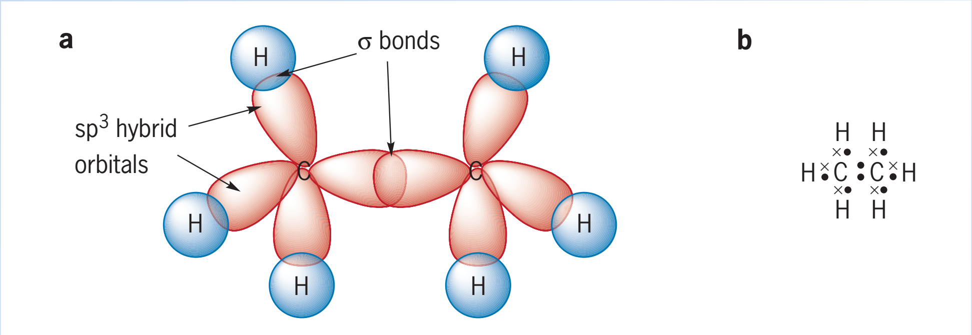


Figure 2.2.8 (a) The σ bonding between sp^3 hybrid orbitals of carbon and s orbitals of hydrogen in ethane. (b) The Lewis structure of ethane.

Example 3: Ammonia, NH_3

In ammonia, nitrogen has 5 electrons in its valence shell and forms three equal bonds with the hydrogen atoms. In addition there is a non-bonding pair of electrons on the nitrogen atom. This must be included in consideration of hybridized orbitals.

The s orbital and three p orbitals of nitrogen mix to form four sp^3 hybrid orbitals; however, one of these four hybrid orbitals is already filled with the non-bonding pair of electrons. The other three hybrid orbitals are able to form σ bonds with three hydrogen atoms. As in VSEPR theory, the 107° bond angles in ammonia can still be explained in terms of the greater repulsion between the non-bonding electron pair and the bonding electron pairs. The ammonia molecule is trigonal pyramidal in shape.

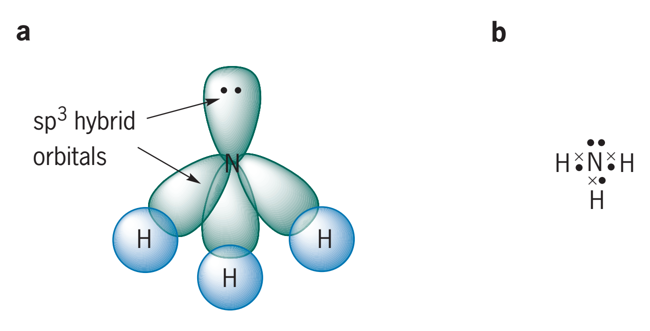


Figure 2.2.9 (a) The σ bonding between sp^3 hybrid orbitals of nitrogen and s orbitals of hydrogen in ammonia. (b) The Lewis structure of ammonia.

Example 4: Hydrazine, N_2H_4

In hydrazine, the two nitrogen atoms share a single covalent bond and each is bonded to two hydrogen atoms. There is a non-bonding pair of electrons on each nitrogen atom. Each of the two nitrogen atoms in hydrazine exhibits sp^3 hybridization.

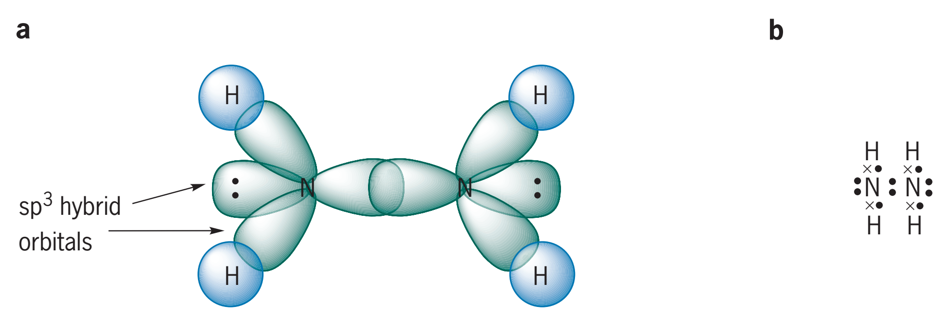


Figure 2.2.10 (a) Hydrazine exhibits σ bonding between sp^3 hybrid orbitals and both s orbitals and other sp^3 orbitals. (b) The Lewis structure of hydrazine.

Example 5: Water, H_2O

In water, oxygen has 6 electrons in its valence shell and forms two equal bonds with the hydrogen atoms. In addition there are two non-bonding pairs of electrons on the oxygen atom. This must be included in consideration of hybridized orbitals.

The s orbital and three p orbitals of oxygen mix to form four sp^3 hybrid orbitals; however, two of these four hybrid orbitals are already filled with non-bonding pairs of electrons. The other two hybrid orbitals are able to form σ bonds with two hydrogen atoms. As in VSEPR theory, the 104.5° bond angles in water can be explained in terms of the greater repulsion between non-bonding electron pairs and bonding electron pairs. The water molecule is V-shaped.

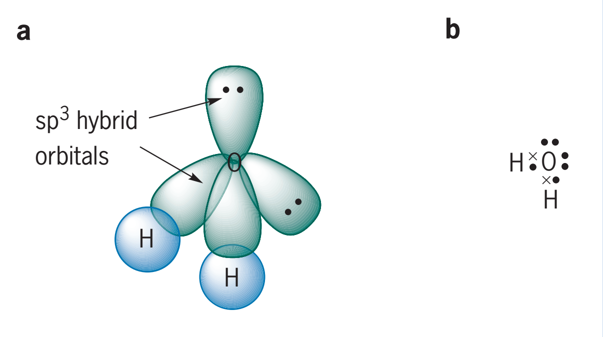


Figure 2.2.11 (a) The σ bonding between sp^3 hybrid orbitals of oxygen and s orbitals of hydrogen in water. (b) The Lewis structure of water.

CHEM COMPLEMENT

Hydrazine and life on Mars

Hydrazine, N_2H_4, is a colourless liquid at room temperature with some similarity to water. Its melting point is 1°C and its boiling point is 114°C. Liquid hydrazine has a density of 1.01 g cm^{-3}. While it is commonly used in the synthesis of other chemicals, a more dramatic use of hydrazine is as a rocket fuel. In World War II, hydrazine was used in mixtures with water, methanol or hydrogen peroxide as a rocket fuel for the Messerschmitt Me 163B, the first and only rocket-powered fighter aircraft used in that war. In more recent times it has been used as the propellent for rocket manoeuvring thrusters, because of its reactions that generate large quantities of hot gas from a small volume of hydrazine.

$$3N_2H_4(l) \rightarrow 4NH_3(g) + N_2(g)$$

$$N_2H_4(l) \rightarrow N_2(g) + 2H_2(g)$$

$$4NH_3(g) + N_2H_4(l) \rightarrow 3N_2(g) + 8H_2(g)$$

Hydrazine has been used in this way in the Viking landers (two spacecraft launched in the 1970s whose mission objectives were to obtain high resolution images of Mars), the NASA space shuttles, and the Phoenix lander, which was launched on 4 August 2007.

The development and launch of the Phoenix lander was a collaborative project between universities from USA, Canada, Switzerland, Denmark and Germany as well as NASA and the Canadian Space Agencies. The lander arrived on Mars on 26 May 2008 and searched for environments suitable for microbial life, including evidence of water—essential to life as we know it.

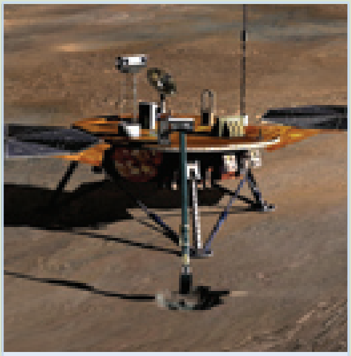


Figure 2.2.12 Hydrazine was used in the thrusters that helped land the Phoenix lander on Mars.

sp^2 hybridization

Boron is an element that only forms three bonds. It has three electrons in its valence shell and will form three covalent bonds with elements such as hydrogen (BH_3) and fluorine (BF_3). These three equal covalent bonds can be explained by the existence of hybrid orbitals. The electron configuration of boron is $1s^2 2s^2 2p^1$. If the 2s orbital and two 2p orbitals are mixed, the hybrid orbitals will be called sp^2 hybrid orbitals. The sp^2 hybrid orbitals will be arranged around the central atom (boron) in such as way as to minimize electrostatic repulsion. This results in a trigonal planar arrangement.

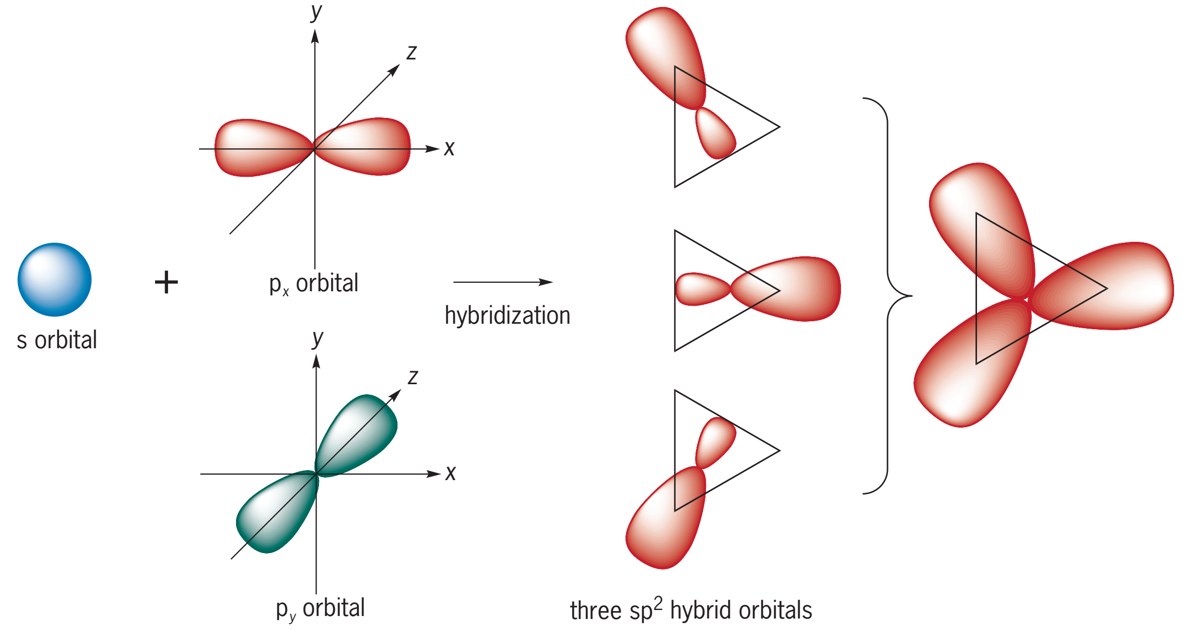


Figure 2.2.13 One s orbital and two p orbitals mix to form three sp^2 hybrid orbitals.

In BH_3 and BF_3 the sp^2 hybrid orbitals can form σ bonds with the 1s orbital of hydrogen and a 2p orbital of fluorine. The H–B–H or F–B–F bond angle will be 120° and the molecule will have a trigonal planar shape.

We can expect sp^2 hybridization to occur whenever there is a trigonal planar arrangement of atoms around a central atom.

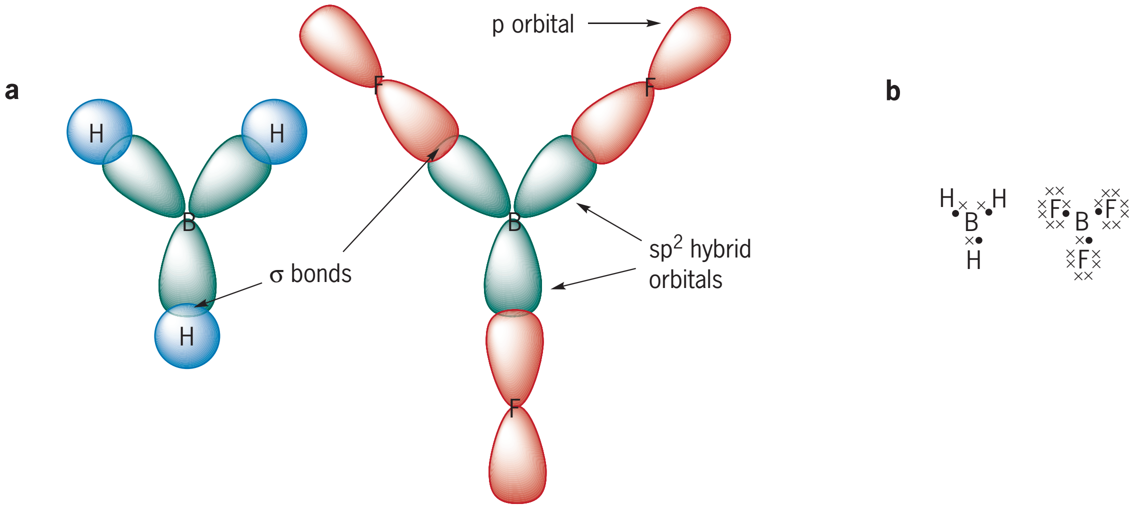


Figure 2.2.14 (a) The sp^2 hybrid orbitals of boron form σ bonds with hydrogen and fluorine. (b) The Lewis structures of BH_3 and BF_3.

Example 6: Ethene

Ethene, C_2H_4, has a C–C double bond between the two carbon atoms and there is a trigonal planar arrangement of atoms around each carbon. Although carbon has four orbitals in the valence shell, only three of them (2s, $2p_x$ and $2p_y$) are involved in the hybridization. The fourth orbital, the $2p_z$ orbital, exists at right angles to the plane of the hybrid orbitals.

The sp^2 hybridized orbitals of the carbon atom in ethene form σ bonds with hydrogen 1s orbitals and with the sp^2 hybridized orbital of the other carbon atom. The atoms are sufficiently close that the $2p_z$ orbitals of the two carbon atoms can overlap sideways forming a π bond. The combination of the σ bond between the two sp^2 hybridized orbitals and the π bond between the two $2p_z$ orbitals creates a double bond between the two carbon atoms.

Interactive Animation
Multiple bonds

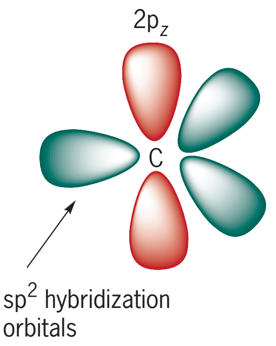


Figure 2.2.15 Each carbon in ethene has three sp^2 hybridized orbitals and a $2p_z$ orbital at right angles to the plane of the sp^2 hybridized orbitals.

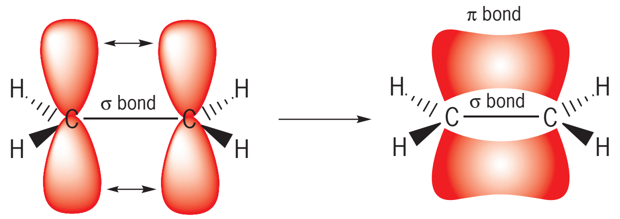


Figure 2.2.16 Formation of π bonding in ethene.

PRAC 2.1
Modelling ethene

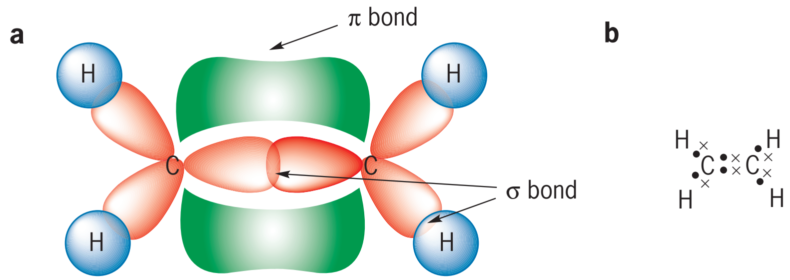


Figure 2.2.17 (a) Formation of σ and π bonds in ethene. (b) Lewis diagram of ethene.

Example 7: Diazene, N_2H_2

This compound has a double bond between the two nitrogen atoms and one hydrogen atom bonded to each nitrogen atom. The two nitrogen atoms exhibit sp^2 hybridization and there is a π bond between the two nitrogen atoms to complete the double bond. The third sp^2 hybrid orbital on each nitrogen atom is occupied by a non-bonding pair of electrons. This results in the molecule having a bent linear shape.

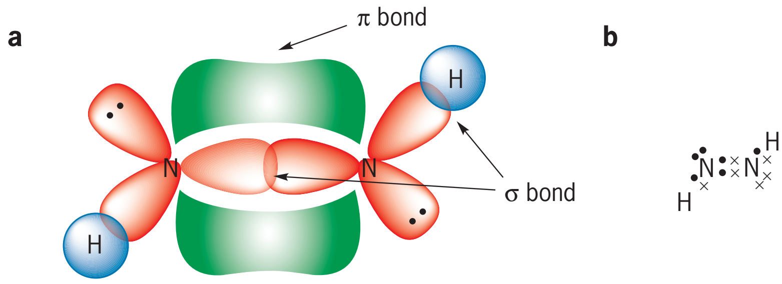


Figure 2.2.18 (a) Formation of σ and π bonds in diazene. (b) Lewis diagram of diazene.

sp hybridization

Beryllium has only two electrons in its valence shell. Its electron configuration is $1s^2 2s^2$. It makes two equal-sized bonds with elements such as hydrogen and the halogens. In order for two equal bonds to be made, the 2s and one 2p orbital must be mixed to form two sp hybrid orbitals. These orbitals will be arranged in such as way as to minimize electrostatic repulsion. This results in a linear arrangement.

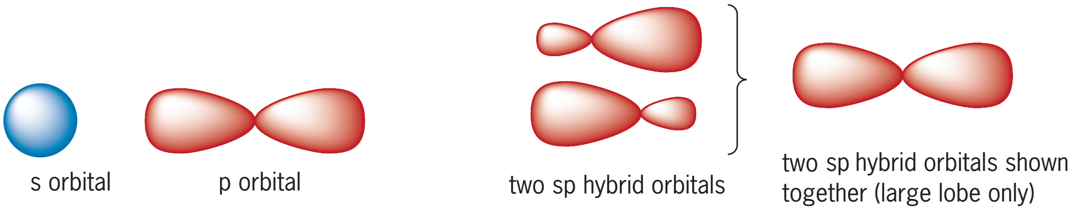


Figure 2.2.19 One s orbital and one p orbital mix to form two sp hybrid orbitals.

In beryllium hydride, BeH_2, the sp hybrid orbitals of beryllium form σ bonds with the 2s orbitals of hydrogen, and in beryllium fluoride, BeF_2, the sp hybrid orbitals of beryllium form σ bonds with the 2p orbitals of fluorine. The H–Be–H and F–Be–F bond angles are both 180°. The shape of these molecules is linear.

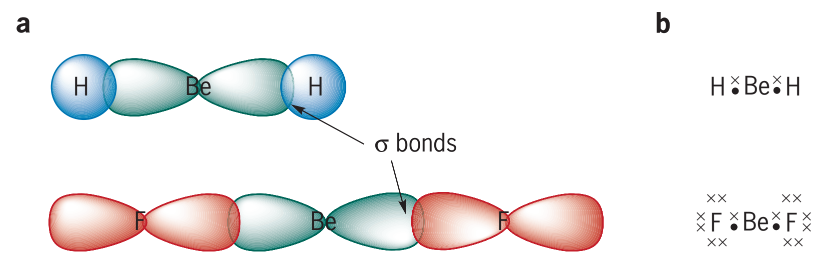


Figure 2.2.20 (a) The sp hybrid orbitals of beryllium form σ bonds with hydrogen and fluorine. (b) The Lewis structures of BeH_2 and BeF_2.

Example 8: Ethyne, C_2H_2

Ethyne, C_2H_2, has a triple bond between the two carbon atoms (C≡C) and there is a linear arrangement of atoms around each carbon. Only two of the valence shell orbitals of carbon (2s, $2p_x$) are involved in the hybridization. The third orbital ($2p_y$) and the fourth orbital ($2p_z$) exist in two different planes to the hybrid orbitals.

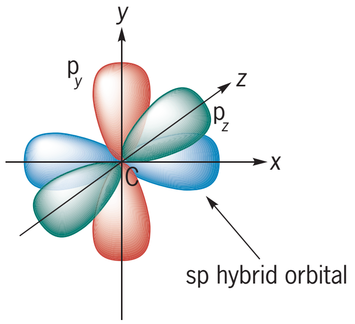


Figure 2.2.21 Each carbon in ethyne has two sp hybridized orbitals, with the $2p_y$ and $2p_z$ orbitals in two different planes to the sp hybridized orbitals.

The sp hybridized orbitals of the carbon atom in ethyne form σ bonds with hydrogen 1s orbitals and with the sp hybridized orbital of the other carbon atom. The atoms are sufficiently close that the $2p_y$ and $2p_z$ orbitals of the two carbon atoms can overlap sideways in planes that are at right angles to each other forming two π bonds. The combination of the σ bond between the two sp hybridized orbitals and the two π bonds between the two $2p_y$ and the two $2p_z$ orbitals creates a triple bond between the two carbon atoms.

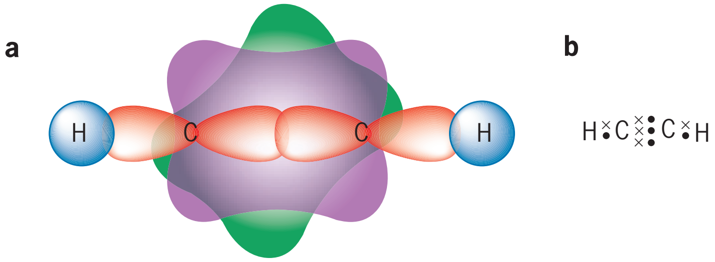


Figure 2.2.22 (a) Formation of σ and π bonds in ethyne. (b) Lewis diagram of ethyne.

WORKSHEET 2.2
Relating bonding to shapes

Example 9: Nitrogen, N_2

In molecules of nitrogen, N_2, the 2s and one 2p orbital of the nitrogen atoms are mixed to form sp hybridized orbitals. One sp hybrid orbital from each atom forms a σ bond between the two atoms and the second sp hybrid orbital on each nitrogen atom is filled by a non-bonding pair of electrons. The remaining p orbitals, p_y and p_z overlap sideways to form π bonds.

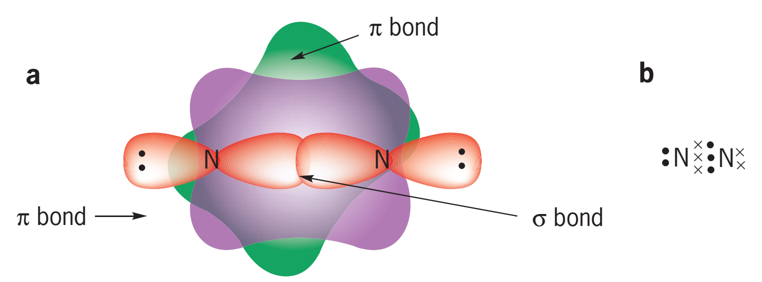


Figure 2.2.23 (a) Formation of σ and π bonds in nitrogen. (b) Lewis diagram of nitrogen.

THEORY OF KNOWLEDGE

In 'On Science and Uncertainty', published in *Discover*, October 1980, Lewis Thomas (1913–1993) an American physician wrote:

> Science is founded on uncertainty. Each time we learn something new and surprising, the astonishment comes with the realization that we were wrong before. The body of science is not, as it is sometimes thought, a huge coherent mass of facts, neatly arranged in sequence, each one logically attached to the next. In truth, whenever we discover a new fact it involves the elimination of old ones. We are always, as it turns out, fundamentally in error.

Scientists do not use the term 'the theory of …' except for those ideas that have been so thoroughly tested that when they are used to explain some phenomena they give the expected result every time. However, we have to be cautious about thinking that theories are absolutely true or have been proven right and assume this status will never change. No matter how many scientists confirm a theory through well-controlled experiments, there is always a possibility that someone one day will be able to extend it, find it limiting, incorrect or even wrong, making each new theory in a sense closer to the truth than the previous one.

- Is it likely that valence bond theory is closer to the truth about how atoms bond than VSEPR theory? Explain.
- Is it possible for a theory to be proposed that has not been experimentally tested and verified?
- If science can never prove anything to be true, why do we trust it so much? A good or 'right' theory is one that appears to work in all the cases that can be found. Can you recall any examples of theories in Chemistry that were once considered 'right' but we now know are 'wrong' or limiting, and 'good' theories that have been replaced by explanations that are even more right?
- In what areas will scientific theories extend in the future? Do you think there is anything that scientific theories will never explain or will science one day give us the answers to everything; nothing will be beyond its scope?

Generally speaking, if there are four negative charge centres around the central atom, the hybridization will be sp^3; if there are three negative charge centres, the hybridization will be sp^2; and if there are two negative charge centres, the hybridization will be sp.

TABLE 2.2.1 SUMMARY OF HYBRIDIZATION

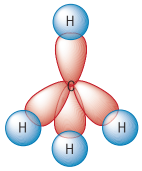
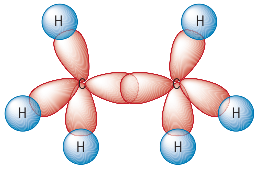
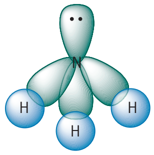
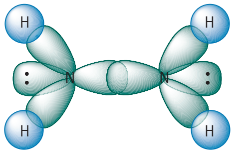
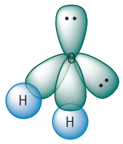
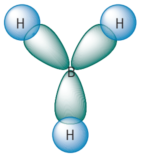
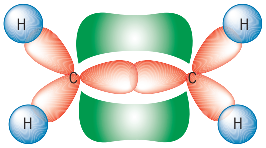
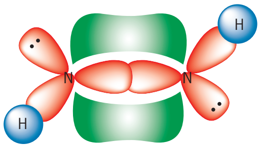
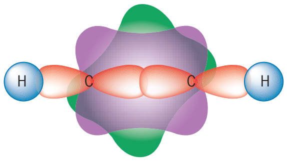
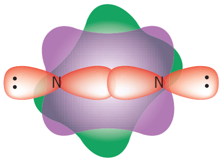
Number of negative charge centres around central atom	Number of non-bonding electron pairs on central atom	Type of hybridization observed	Example	Description of bonding between atoms
4	0	sp^3	**Methane, CH_4** 	σ bonds between sp^3 hybrid orbitals of carbon and s orbital of hydrogen
4	0	sp^3	**Ethane, C_2H_6** 	σ bonds between sp^3 hybrid orbitals of carbon and s orbital of hydrogen AND sp^3 hybrid orbitals of the two carbon atoms
4	1	sp^3	**Ammonia, NH_3** 	σ bonds between sp^3 hybrid orbitals of nitrogen and s orbital of hydrogen
4	1	sp^3	**Hydrazine, N_2H_4** 	σ bonds between sp^3 hybrid orbitals of nitrogen and s orbital of hydrogen AND sp^3 hybrid orbitals of the two nitrogen atoms
4	2	sp^3	**Water, H_2O** 	σ bonds between sp^3 hybrid orbitals of oxygen and s orbital of hydrogen
3	0	sp^2	**Borane, BH_3** 	σ bonds between sp^2 hybrid orbitals of boron and s orbital of hydrogen

TABLE 2.2.1 SUMMARY OF HYBRIDIZATION (continued)

Number of negative charge centres around central atom	Number of non-bonding electron pairs on central atom	Type of hybridization observed	Example	Description of bonding between atoms
3	**0**	sp^2	**Ethene, C_2H_4** 	σ bonds between sp^2 hybrid orbitals of carbon and s orbital of hydrogen, σ bond between sp^2 hybrid orbitals of the two carbon atoms AND π bonds between two carbon atoms
3	1	sp^2	**Diazene, N_2H_2** 	σ bonds between sp^2 hybrid orbitals of nitrogen and s orbital of hydrogen, σ bond between sp^2 hybrid orbitals of the two nitrogen atoms AND π bonds between two nitrogen atoms
2	0	sp	**Beryllium dihydride, BeH_2** 	σ bonds between sp hybrid orbitals of beryllium and s orbital of hydrogen
2	0	sp	**Ethyne, C_2H_2** 	σ bonds between sp hybrid orbitals of carbon and s orbital of hydrogen, σ bond between sp hybrid orbitals of the two carbon atoms AND two π bonds between two carbon atoms.
2	1	sp	**Nitrogen, N_2** 	σ bond between sp hybrid orbitals of the two nitrogen atoms AND two π bonds between two nitrogen atoms

Section 2.2 Exercises

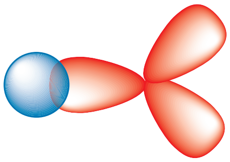
1 Both σ (sigma) and π (pi) bonds involve the overlapping of orbitals. Draw a diagram to show the difference between the overlapping that constitutes a σ bond and the overlapping to make a π bond.

2 Copy and complete the following table to give an example and to indicate what type of bond could occur between the orbitals or hybrid orbitals listed.

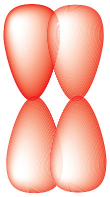
Orbital 1	**Orbital 2**	**Example of molecule in which the bond occurs**	**σ bond? (yes/no)**	**π bond? (yes/no)**
s orbital	s orbital	H_2		
s orbital	sp hybrid orbital			
p orbital	p orbital			
sp^3 hybrid orbital	sp^2 hybrid orbital			

3 Consider the following diagrams and state whether they are illustrating a σ bond or a π bond.

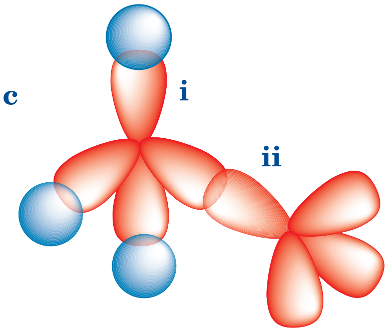
a



b



c



4 Use the concepts of σ and π bonding to explain why a carbon–carbon double bond is not twice as strong as a carbon–carbon single bond.

5 State the type of hybridization that would be occurring in order for the following geometry to occur around the central atom.

a trigonal planar

b linear

c tetrahedral

6 Considering the bonding between two carbon atoms, outline how each of the following bonds are formed.

a a single bond

b a double bond

c a triple bond

7 Describe the type of bonding and any hybridization involved in the bond between the carbon atom and the nitrogen atom in hydrogen cyanide, HCN.

8 Describe the hybridization of the nitrogen atom in ammonia.

9 The carbon atom in a molecule of methane, CH_4, is sp^3 hybridized. Explain how the geometry of the sp^3 hybridization agrees with that suggested by the Lewis structure of methane.

10 The carbon atom in carbon dioxide, CO_2, makes both sigma and pi bonds with the oxygen atoms. Describe the hybridization of orbitals around the carbon atom and around the oxygen atoms, and describe how the sigma and pi bonds are formed with oxygen. In your answer you should also account for any non-bonding pairs of electrons.

2.3 DELOCALIZATION OF ELECTRONS

In the previous section we saw that the Lewis structures of the molecules agreed with the structure explained by hybridization. However, not all molecular structures can be represented by just one Lewis structure.

Resonance structures

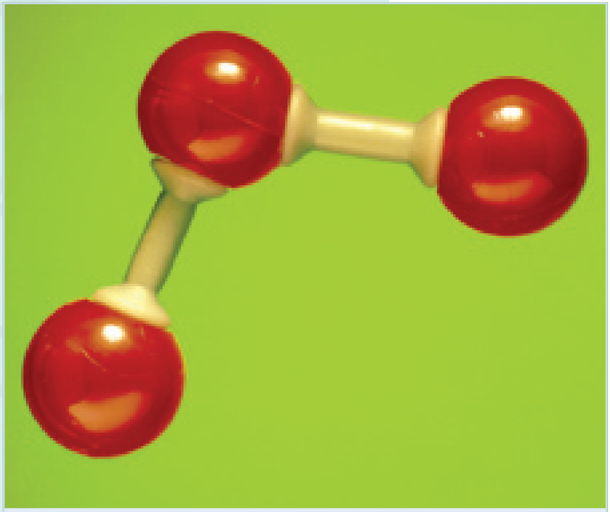


Figure 2.3.1 A molecular model of ozone with two equal length bonds.

In the case of some molecules and ions, the experimentally determined arrangement of atoms is not adequately described by a single Lewis structure. Usually in such cases, experimental measurements have determined the bond lengths of two or more bonds to be equal, yet it is not possible to construct one Lewis structure that represents this information. Ozone, O_3, is one such molecule.

Each oxygen atom in ozone has six valence electrons and needs to make two bonds to complete the valence octet, yet if two of the oxygen atoms each make two bonds, the third will need to make four bonds and this is not possible. A Lewis structure in which there is one O–O single bond and one O–O double bond meets the requirements of eight valence electrons on each oxygen atom; however, this does not match the experimental measurements. To explain the two equal O–O bond lengths of 0.128 nm we can use **resonance structures**.

A set of resonance structures shows a number of Lewis structures that are equivalent, having exactly the same placement of atoms, but differing placement of electrons; that is, double and single bonds are interchanged. Neither Lewis structure on its own truly represents the molecule; however, a blend of the two Lewis structures does the job well. The resonance structures of ozone are shown below. The double-headed arrow is used to indicate that the real molecule is described by an average of the two resonance structures. This average of the two structures is called a **resonance hybrid**.

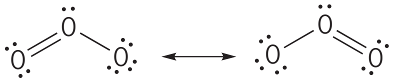


Figure 2.3.2 There are two resonance structures of ozone.

Other molecules whose Lewis structures are best represented as a set of resonance structures include benzene (C_6H_6) and the nitrate (NO_3^-), nitrite (NO_2^-), carbonate (CO_3^{2-}) and carboxylate ($RCOO^-$) ions.

Example 1: Nitrate ion, NO_3^-

There are three equivalent Lewis structures that can be drawn for the nitrate ion. In each case the arrangement of atoms is the same, but the placement of electrons differs. All three Lewis structures, when taken together, describe the nitrate ion in which all three N–O bond lengths are the same.

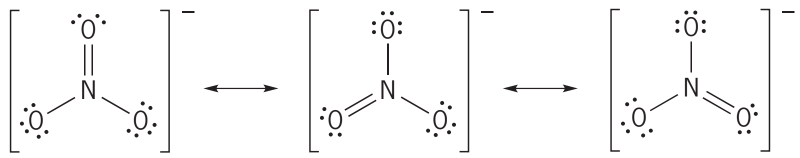


Figure 2.3.3 There are three resonance structures of the nitrate ion, NO_3^-.

Example 2: Nitrite ion, NO_2^-

With one less oxygen atom than the nitrate ion, the nitrogen atom in nitrite has a non-bonding pair of electrons and a double and a single bond to the two oxygen atoms. There are two equivalent Lewis structures for the nitrite ion.

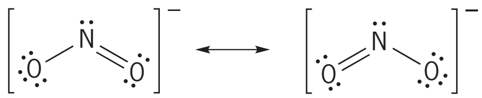


Figure 2.3.4 There are two resonance structures of the nitrite ion, NO_2^-.

Example 3: Carbonate ion, CO_3^{2-}

The three resonance structures for the carbonate ion are very similar to those for the nitrate ion except that the ion has a 2– charge, rather than the 1– charge of the nitrate ion.

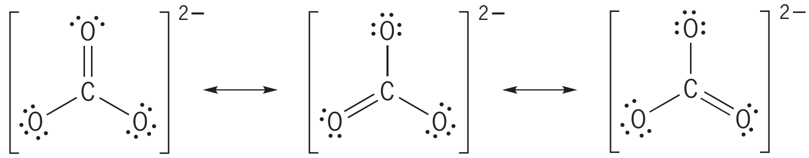


Figure 2.3.5 There are three resonance structures of the carbonate ion, CO_3^{2-}.

Example 4: Ethanoate ion, CH_3COO^-

The ethanoate ion is typical of a carboxylate ion, formed when a carboxylic acid donates a hydrogen ion in an acid–base reaction. While two resonance structures are possible for any carboxylate ion, note that when the acidic hydrogen atom is in place on the carboxylic acid, the C–O bond lengths are actually different, since they are locked in place as a C–O double bond and a C–O single bond.

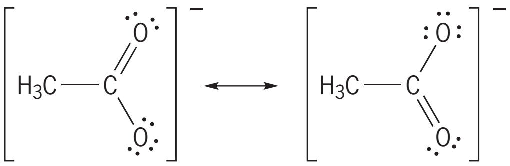


Figure 2.3.6 There are two resonance structures of the ethanoate ion, CH_3COO^-.

Example 5: Benzene, C_6H_6

In 1865, Friedrich August Kekulé von Stradonitz proposed that the structure of benzene was that of a single ring of six carbon atoms with alternating single and double C–C bonds. The length of the C–C bonds in benzene were found using X-ray crystallography to actually be equal in length (0.139 nm).
To represent the true structure, benzene can be drawn as two resonance structures; once again remembering that resonance structures have the same arrangement of atoms but different placement of electrons.

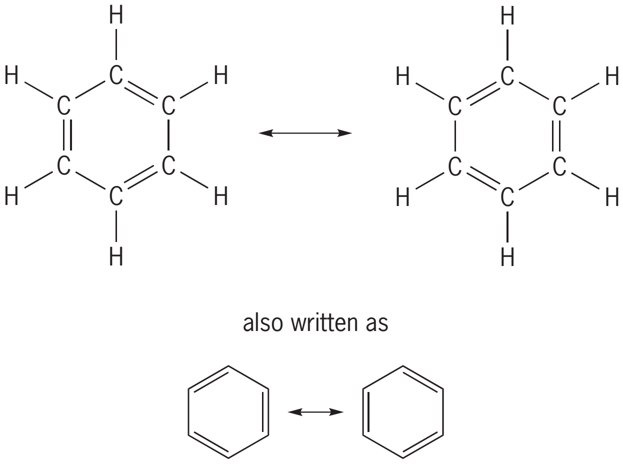


Figure 2.3.7 There are two resonance structures of benzene, C_6H_6.

CHEM COMPLEMENT

Dame Kathleen Lonsdale

Kathleen Yardley was born in Ireland in 1903. She was educated in England, graduating in Physics from University College, London, in 1924. After graduating, she worked on molecular structure using X-ray crystallography in the research team of Sir William Bragg, also at University College. Kathleen married Thomas Lonsdale in 1927 and combined her work in science with motherhood, having three children. As a pacifist, she refused to become involved in civil defence duties during World War II, and was imprisoned.

Her work in X-ray crystallography confirmed the structure of benzene as being that of a planar hexagonal ring of carbon atoms. Later work in X-ray diffraction measured all of the bond lengths in benzene to be the same. She also worked on the synthesis of diamond and lonsdaleite, a rare form of diamond found in meteorites, was named in her honour.

In 1949, Kathleen Lonsdale was made professor of Chemistry at University College, London, and as such was the first female professor at that College.

Figure 2.3.8 Dame Kathleen Lonsdale (1903–1971).

THEORY OF KNOWLEDGE

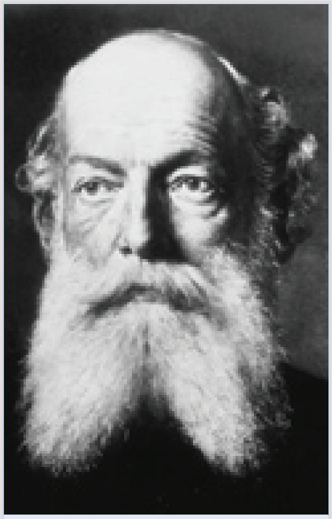


Figure 2.3.9 Friedrich August Kekulé von Stradonitz (1829–1896) discovered the ring structure of benzene.

Sometimes to make a scientific breakthrough, no matter how well tested the idea, you need to be able to think creatively. For German chemist Friedrich August Kekulé (1829–1896), the inspiration for his ‘out of the box’ thinking came from a dreamlike vision he had when he dozed off while thinking about the benzene molecule.

Up until 1858 chemists did not really know what organic molecules looked like at the molecular level.

Kekulé, a theoretical chemist, was particularly curious as to why benzene, the liquid manufactured from whale oil and used for lighting, has such unusual chemical properties. Without a clear understanding of its structure, an explanation seemed impossible. One day while travelling home on the bus from his laboratory, he dozed off and in his dream saw benzene molecules twisting and turning in a snake-like motion.

One of the snakes caught hold of its tail and made a ring-like formation. When he woke he had a flash of inspiration, and as soon as he got home he made sketches of his dream form of benzene. In 1865 Kekulé presented a paper to the Royal Academy of Belgium, proposing that the structure of benzene was a single hexagonal ring of six carbon atoms with alternating single and double carbon–carbon bonds. His theory met widespread approval from fellow chemists.

However Kekulé’s structure did not stand the test of time. It wasn’t long before modern X-ray diffraction techniques gave chemists a deeper understanding of cyclic compounds, revealing that the carbon–carbon bonds in benzene were actually equal in length.

Further experiments provided evidence that Kekulé’s alternating single and double bonds were not possible. First, benzene underwent substitution reactions instead of the addition reactions you would expect of a molecule with three double bonds (*Chemistry: For use with the IB Diploma Programme Standard Level*, p. 376). Furthermore, Hess’s law data based on the hydrogenation of cyclohexene gave an expected enthalpy change of –360 kJ mol^{-1} for Kekulé’s structure, while that of benzene was –208 kJ mol^{-1}, suggesting that benzene had a more stable structure.

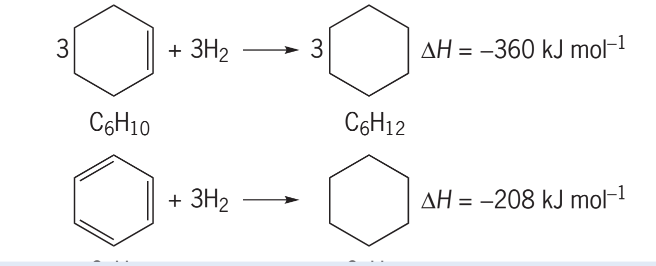


Figure 2.3.10 A comparison between the hydrogenation of cyclohexene and that of benzene.

The emergence of these problems resulted in Kekulé’s structure being replaced by a truer ‘resonance hybrid’ structure of benzene with the same arrangement of atoms but with the length of each C–C bond being somewhere between that of a single and a double bond.

- Kekulé was more of a theoretical than experimental chemist. Distinguish between the two.
- Kekulé was a talented linguist and artist, and his parents wanted him to become an architect. How do you think his experiences of language and art might have helped him as a chemist?
- Kekulé’s story demonstrates that being able to make connections between seemingly unrelated phenomena can lead to significant advances in science. Since we can’t rely entirely on inductive or deductive reasoning as a way of knowing, scientists need to be able to tap into other creative ways of thinking. Edward de Bono is regarded by many as the leading authority in the field of creative thinking. What do you think de Bono meant when he said ‘Logic is the tool that is used to dig a hole deeper and bigger, but if a hole is in the wrong place, then no amount of digging will get you to your intended destination.’

AS **14.3.1 Describe the delocalization of π electrons and explain how this can account for the structures of some species. © IBO 2007**

WORKSHEET 2.3
Delocalization of electrons

Delocalization of electrons (resonance)

The molecules and ions that require sets of Lewis resonance structures to describe them can be accurately described in terms of hybridization of orbitals. Recall that π bonds were found to accommodate the second pair of electrons in a double bond such as the C–C double bond found in ethene, C_2H_4. In this case the bonding electrons in the π bond can be described as **localized electrons,** as they are restricted to the confines of region between the two carbon atoms. The equal length C–C bonds in benzene can also be described in terms of π bonds, but these electrons are **delocalized**. The distribution of electrons within a π bond can be called **resonance**, or the concept of resonance. This seems easy to confuse with the term 'resonance structures'; however, it is important to note the context in which the term is being used.

Example 1: Benzene

In a benzene molecule, the six carbon atoms are arranged in a ring in which the geometry around each carbon atom is trigonal planar. The C–C–H bond angle is 120°. The hybridization that matches this geometry is sp^2, so we can deduce that each carbon atom has one 2s orbital and two 2p orbitals mixed together to make three sp^2 hybrid orbitals. The third p orbital of each carbon is perpendicular to the plane of the sp^2 hybrids and has one electron in it. These six p orbitals form a π bond right around the benzene ring, and the six unpaired electrons are delocalized within this π bond. This equality of bonds in benzene agrees with the experimentally determined bond length of 0.139 nm.

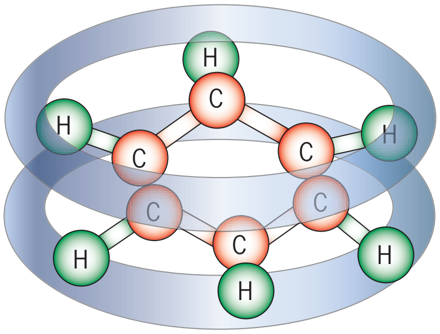


Figure 2.3.11 The six unpaired electrons can be represented in a delocalized π bond in the benzene ring.

Example 2: Nitrate ion, NO_3^-

In the nitrate ion, the nitrogen atom has a trigonal planar geometry, so we can assign sp^2 hybridization to it. In addition, each oxygen atom will also be sp^2 hybridized, with two pairs of non-bonding electrons occupying two of the three hybrid orbitals. A σ bond exists between the nitrogen and oxygen atoms and in addition to the extra electron which gives the ion a negative charge, the last electron in each atom occupies a p orbital perpendicular to the plane of the sp^2 hybrid orbitals. These p orbitals create a delocalized π bond.

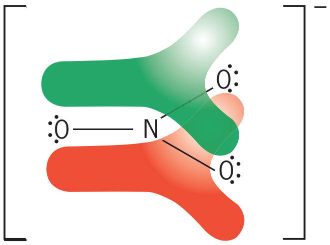


Figure 2.3.12 The unpaired electrons can be represented in a delocalized π bond in the nitrate ion.

Example 3: Nitrite ion, NO_2^-

The nitrite ion has a bent linear geometry, due to the presence of the non-bonding pair of electrons on the nitrogen atom. We can assign sp^2 hybridization to it. In addition, each oxygen atom will also be sp^2 hybridized, with two pairs of non-bonding electrons occupying two of the three hybrid orbitals. A σ bond exists between the nitrogen and oxygen atoms and, in addition to the extra electron that gives it the negative charge, the last electron in each atom occupies a p orbital perpendicular to the plane of the sp^2 hybrid orbitals. These p orbitals create a delocalized π bond.

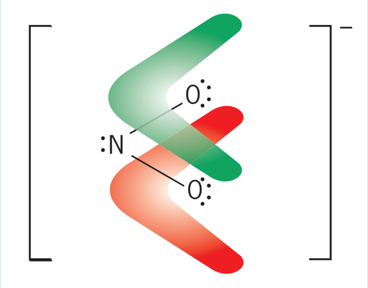


Figure 2.3.13 The unpaired electrons can be represented in a delocalized π bond in the nitrite ion.

Example 4: Carbonate ion, CO_3^{2-}

In the carbonate ion, the carbon atom has a trigonal planar geometry, so we can assign sp^2 hybridization to it. In addition, each oxygen atom will also be sp^2 hybridized, with two pairs of non-bonding electrons occupying two of the three hybrid orbitals. A σ bond exists between the carbon and oxygen atoms and, in addition to the extra two electrons that give it the 2– charge, the last electron in each atom occupies a p orbital perpendicular to the plane of the sp^2 hybrid orbitals.These p orbitals create a delocalized π bond.

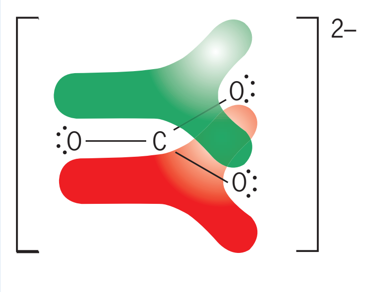


Figure 2.3.14 The six unpaired electrons can be represented in a delocalized π bond in the carbonate ion.

Example 5: Ethanoate ion, CH_3COO^-

In the ethanoate ion, the carbon atom in the carboxylate ion (COO^-) has a trigonal planar geometry, so we can assign sp^2 hybridization to it. In addition, each oxygen atom will also be sp^2 hybridized, with two pairs of non-bonding electrons occupying two of the three hybrid orbitals. A σ bond exists between the carbon and oxygen atoms and, in addition to the extra electron that gives it the negative charge, the last electron in each atom occupies a p orbital perpendicular to the plane of the sp^2 hybrid orbitals. These p orbitals create a delocalized π bond.

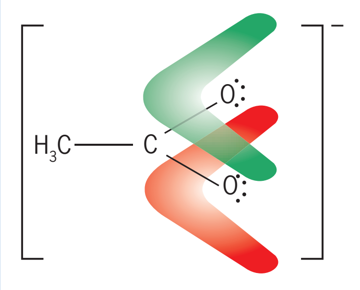


Figure 2.3.15 The four unpaired electrons can be represented in a delocalized π bond in the ethanoate ion.

Section 2.3 Exercises

1 Explain why resonance structures were found to be necessary for molecules and ions such as C_6H_6 and CH_3COO^-.

2 Draw the resonance structures of:

a $HCOO^-$

b NO_3^-

c SO_4^{2-}

3 Describe how you would expect the actual sulfur–oxygen bond lengths in SO_4^{2-} to compare with a sulfur–oxygen single bond and a sulfur–oxygen double bond.

4 **a** State the names of two molecules in which delocalized electrons may be found.

b Name the type of obitals in which delocalized electrons are found.

5 **a** State which of the following molecules or ions will exhibit delocalized bonding: SO_3^{2-}, H_2CO, O_3, NH_4^+.

b Draw the resonance structures of the molecules or ions that exhibit delocalized bonding.

6 **a** Use the concept of resonance to explain why the six carbon–carbon bonds in benzene are of equal length.

b Explain why the structure of benzene is drawn as a hexagon with a ring inside it, when the concept of resonance is being considered.

7 Naphthalene, $C_{10}H_8$, is a molecule made up of two six-membered rings with one shared side.

a Draw two Lewis resonance structures for naphthalene.

b The observed carbon–carbon bond lengths in naphthalene are shorter than carbon–carbon single bonds and longer than carbon–carbon double bonds. Explain this observation using the concept of resonance.

c Represent the resonance in naphthalene in a way that is analogous with that used to represent resonance in benzene.

8 **a** State and explain whether the π bond in CH_3COO^- is localized or delocalized.

b State and explain whether the π bond in CH_3COOH is localized or delocalized.

Chapter 2 Summary

Terms and definitions

Axial position Atoms arranged above and below a central atom in a molecule.

Delocalized electrons Electrons that are free to move within a pi (π) bond.

Equatorial position Atoms arranged around the middle of a molecule at right angles to those in the axial position.

Hybridization The process of mixing atomic orbitals as atoms approach each other.

Hybrid orbitals Orbitals formed when atomic orbitals in the valence shell of an atom are mixed together.

Localized electrons Electrons in a pi (π) bond which cannot move beyond the two bonding atoms.

Negative charge centres Pairs of bonding or non-bonding electrons around a central atom.

Octahedral (or square bipyramidal) A molecular shape (geometry) in which six atoms surround a central atom, with four in an equatorial plane and two in axial positions.

Octahedron A shape with eight faces, eight edges and six vertices.

Octet rule That the valence shell of an atom should contain no more than 8 electrons.

Orbital diagram A diagrammatic representation of electron configuration showing electrons as ↑ and ↓ in boxes.

Pi (π) bond Bond between two atoms formed by the sideways overlapping of two orbitals (usually *p* orbitals).

Resonance The concept of electrons being delocalized in a pi (π) bond rather than being bound in a double bond.

Resonance hybrid The average of two resonance structures, which represents the observed molecule accurately.

Resonance structures Different Lewis structures of the same molecule in which double and single bonds alternate.

Sigma (σ) bond Bond between two atoms formed by the end to end overlapping of two orbitals.

Square bipyramidal *see* Octahedral.

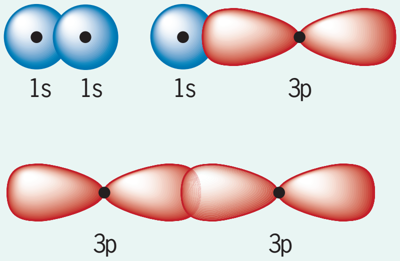
Square planar A molecular shape (geometry) in which four atoms surround a central atom in a plane.

Trigonal bipyramid A molecular shape (geometry) in which five atoms surround a central atom, with three in an equatorial plane and two in axial positions.

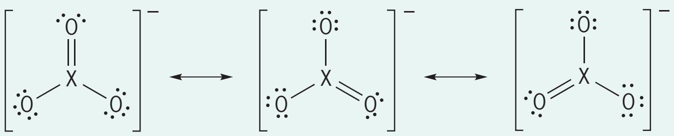
Valence-bond theory A theory in which regions of electron density between two atoms is explained in terms of the overlap of two atomic orbitals.

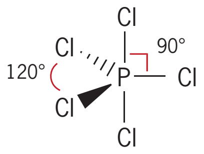
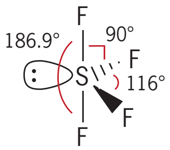
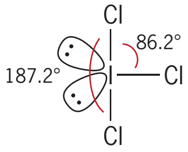
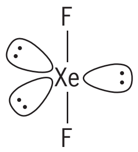
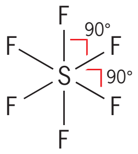
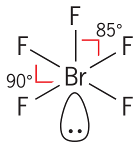
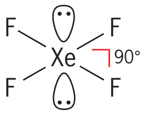
Concepts

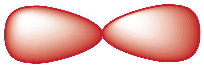
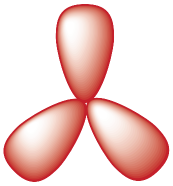
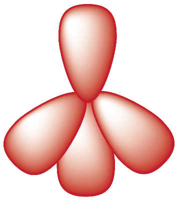
- Lewis structures (electron dot diagrams) and valence structures can be used to represent molecules with five or six negative charge centres.
- The VSEPR (**v**alence **s**hell **e**lectron **p**air **r**epulsion) model is used in determining the shapes of molecules and angles between the atoms in a molecule (see table 2.4.1).
- In valence-bond theory, bonds are formed by the overlapping of orbitals. Such orbitals may form sigma (σ) bonds or pi (π) bonds.



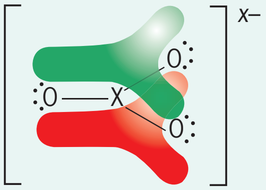
- Sigma bonds result in the formation of single covalent bonds.
- Pi bonds, together with sigma bonds, result in the formation of double and triple covalent bonds.
- Hybrid orbitals are formed by the mixing of two or more atomic orbitals, and support evidence of numbers of equal bonds around a central atom.
- Hybrid orbitals are named according to the orbitals that are mixed together to form them.
- Resonance structures are used to accurately represent a molecule for which one structure is not sufficient.



Number of negative charge centres	**Number of bonding electron pairs**	**Number of non-bonding electron pairs**	**Shape of molecule**	**Example**	**Diagram of shape**
5	5	0	Trigonal bipyramid	PCl_5	
5	4	1	Seesaw	SF_4	
5	3	2	T-shaped	IF_3	
5	2	3	Linear	XeF_2	
6	6	0	Octahedral or square bipyramidal	SF_6 PF_6^-	
6	5	1	Square pyramidal	BrF_5	
6	4	2	Square planar	XeF_4	

Hybrid orbital	Formed by	No. of negative charge centres	Shape
sp	**One** s orbital and **one** p orbital	2	Linear 
sp^2	**One** s orbital and **two** p orbitals	3	Trigonal planar 
sp^3	**One** s orbital and **three** p orbitals	4	Tetrahedral 

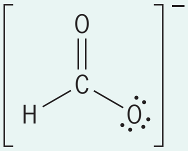
- Hybrid orbitals, together with pi bonds containing delocalized electrons, can be used to accurately represent the molecules for which resonance structures were used.



Chapter 2 Review questions

1 Draw each of the following molecules and state their shape according to VSEPR theory.

- **a** SF_6
- **b** BrF_3
- **c** ICl_4^-
- **d** XeF_2
- **e** $TeCl_4$



2 One of the resonance structures of the methanoate ion is shown:

The bond angles in this ion are exactly 120°. According to VSEPR theory, multiple bonds repel other negative charge centres more strongly than do single bonds. Use this information to discuss whether the observed bond angles are consistent with this resonance structure of the methanoate ion.

3 **i** State the number of negative charge centres about a central atom, given the following bond angles in the molecule.

ii Name the shape of each molecule.

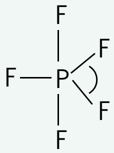
- **a** 120°
- **b** 180°
- **c** 109.5°
- **d** 90°

4 Draw a molecule for each of the following descriptions, showing the shape clearly.

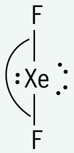
- **a** A group 5 element with six halogen atoms bonded to it and an overall negative charge (YX_6^-)
- **b** A group 0 element with four halogen atoms bonded to it and two non-bonding pairs of electrons (ZX_4)
- **c** A group 5 element with five halogen atoms bonded to it (YX_5)
- **d** A group 7 element with three halogen atoms bonded to it and one non-bonding pair of electrons (WX_3)

5 State the value for the indicated bond angle in the following molecules.

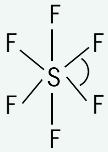
a



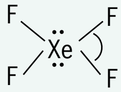
b



c



d



6 **a** Draw the Lewis structure of:

i BrF_4^- **ii** BF_4^-

b Explain why BrF_4^- is not the same shape as BF_4^-.

7 **a** Compare the shapes of the two molecules XeF_2 and BrF_2^+ by drawing each one.

b Explain why the shapes are different, although there are only two atoms bonded to the central atom in each case.

8 **a** Outline the meaning of the term *orbital overlap*.

b Describe the significance of orbital overlap in valence-bond theory.

9 Copy and complete the following table relating molecular shape to hybridization of orbitals.

Bond angle	Hybridization of orbitals	Shape (name and draw)
120°		
180°		
109.5°		

10 State the hybridization of the central atom in:

a BCl_3

b $AlCl_4^-$

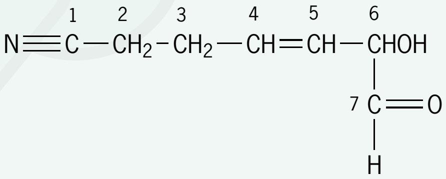
c CS_2

11 Identify the carbon atom/s in the structure below that has the following hybridizations.

a sp

b sp^2

c sp^3



$N\equiv C-CH_2-CH_2-CH=CH-CHOH$, with $C(=O)H$ below

12 The nitrogen atoms in N_2 participate in multiple bonding, whereas those in hydrazine, N_2H_4, do not. Explain this observation by considering the hybridization of the nitrogen atoms in the two molecules.

13 State the hybridization of the bolded atom in each of the following molecules.

a $\mathbf{C}O_2$

b $H_2\mathbf{C}O$

c $CH_3\mathbf{N}H_2$

14 For each of the following molecules:

i Draw the structure of the molecule.

ii Describe the hybridization of each carbon atom in the molecule.

iii State whether the bonding between the pairs of carbon atoms in the molecule involves σ or π bonds.

a propene, C_3H_6

b methyl benzene, $C_6H_5CH_3$

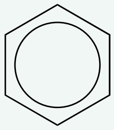
c 2-methylbut-2-ene, $CH_3C(CH_3)CHCH_3$

15 If the O–O bonds in ozone can be described as 'one and a half bonds', describe the S–O bonds in SO_3^{2-} in a similar way.

16 Squalene is a hydrocarbon with the molecular formula $C_{30}H_{50}$. It is obtained from shark liver and also from some botanical sources such as wheat germ and olives. It does not have a cyclic structure. Calculate the number of π bonds contained in squalene.

17 Explain why resonance structures can be drawn for the sulfate ion, SO_4^{2-}, but not for the hydrogen sulfate, H_2SO_4, molecule.

18 Draw the two resonance structures of benzene, C_6H_6. How do these structures differ from the structure shown?



19 State how many electrons are involved in the π bond in each of the following molecules or ions.

a CO_3^{2-}

b C_2H_4

c C_6H_6

d NO_2^-

20 Explain why Lewis resonance structures and hybridized structures showing delocalized π electrons can both be correct for a given molecule or ion, such as, CH_3COO^-.

Web Destinations www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 2 Test

Part A: Multiple-choice questions

1 Which molecule is square planar in shape?

A XeO_4

B XeF_4

C SF_4

D SiF_4

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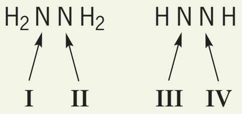
2 What is the hybridization of nitrogen atoms I, II, III and IV in the following molecules?



	I	II	III	IV
A	sp^2	sp^2	sp^3	sp^3
B	sp^3	sp^3	sp^2	sp^2
C	sp^2	sp^2	sp	sp
D	sp^3	sp^3	sp	sp

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3 What is the shape of the species ICl_4^-?

A pyramidal

B square planar

C tetrahedral

D octahedral

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4 Identify the types of hybridization shown by the carbon atoms in the molecule $CH_3CH_2CH_2COOH$.

I sp

II sp^2

III sp^3

A I and II only

B I and III only

C II and III only

D I, II and III

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5 Which is the smallest bond angle in the PF_5 molecule?

A 90°

B 109.5°

C 120°

D 180°

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6 Which statements correctly describe the NO_2^- ion?

I It can be represented by resonance structures.

II It has two lone pairs of electrons on the N atom.

III The N atom is sp^2 hybridized.

A I and II only

B I and III only

C II and III only

D I, II and III

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7 Which statement is correct about multiple bonding between carbon atoms?

A Double bonds are formed by two π bonds.

B Double bonds are weaker than single bonds.

C π bonds are formed by overlap between s orbitals.

D π bonds are weaker than sigma bonds.

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8 NO_3^- is trigonal planar and NH_3 is trigonal pyramidal. What is the approximate hybridization of N in each of the species?

	N in NO_3^-	N in NH_3
A	sp^2	sp^3
B	sp^2	sp^2
C	sp^3	sp^2
D	sp^3	sp^3

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9 Consider the following statements.

I All carbon–oxygen bond lengths are equal in CO_3^{2-}.

II All carbon–oxygen bond lengths are equal in CH_3COOH.

III All carbon–oxygen bond lengths are equal in CH_3COO^-.

Which statements are correct?

A I and II only

B I and III only

C II and III only

D I, II and III

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10 Which species is/are sp^2 hybridized?

- **I** C_2H_4
- **II** C_2H_6
- **III** C_3H_6

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

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 **a** Explain the meaning of the term *hybridization*.
(1 mark)

b State the type of hybridization shown by the carbon atom in the H–C≡N molecule, and the number of σ and π bonds present in the C≡N bond.
(2 marks)

c Describe how σ and π bonds form.
(4 marks)

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2 **a** Draw the Lewis structures for the compounds XeF_4, PF_5 and BF_4^-.
(3 marks)

b Use the valence shell electron pair repulsion (VSEPR) theory to predict the shapes of the three compounds in part **a**. State and explain the bond angles in each of the three compounds.
(3 marks)

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3 By referring to the N_2H_2 molecule describe how sigma (σ) and pi (π) bonds form and describe how single and double bonds differ.
(4 marks)

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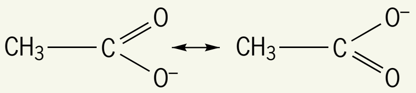
4 The structure of the ethanoate ion can be written as shown below.



The stability of the ethanoate ion suggests a different type of carbon to oxygen bond. Decribe the actual carbon to oxygen bond in the ethanoate ion.
(2 marks)

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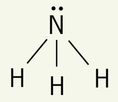
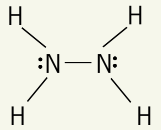
Part C: Data-based question

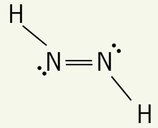
Nitrogen forms a number of different compounds including:

NH_3, H_2NNH_2, HNNH

The structures of the above compounds are:







a Explain the bond angles in H_2NNH_2 and HNNH.
(2 marks)

b Give the hybridization of the nitrogen in NH_3, H_2NNH_2 and HNNH.
(3 marks)

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Part D: Extended-response question

a Draw the Lewis structures, state the shapes and predict the bond angles for the following species.

- **i** PCl_5
(3 marks)
- **ii** SCl_2
(3 marks)
- **iii** ICl_4^-
(3 marks)

b **i** Compare how atomic orbitals overlap in the formation of sigma (σ) and pi (π) bonds.
(2 marks)

ii State the number of sigma bonds and pi bonds in $H_2CC(CH_3)CHCH_2$.
(2 marks)

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Total marks: 47

3 PERIODICITY

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 13: Periodicity.

By the end of this chapter, you should be able to:

- describe the physical state and the electrical conductivity of the period 3 chlorides and oxides, and explain it in terms of their bonding and structures
- describe the reactions of the period 3 chlorides and of chlorine with water
- describe the characteristic properties of the transition elements
- use the differences in properties between scandium and zinc and other d-block elements to explain why scandium and zinc are not considered to be transition elements
- explain why transition elements exist in a range of oxidation states
- explain why transition metal compounds exhibit a range of different colours
- define the term *ligand*
- describe how complexes are formed from ligands and transition metal ions
- list some common catalysts that are transition metals or their compounds, including those used in the Haber process and the Contact process.

IBO Assessment statements 13.1.1 to 13.2.8

Periodicity is the term used for how the properties of elements are repeated, depending on their location in the periodic table. You will recall that the periodic table is divided into vertical columns called groups and horizontal rows called periods. Between groups 2 and 3 is a large block of elements called the *transition metals*. In this chapter we will investigate the properties of the compounds formed by period 3 elements, and we will also look closely at the properties of the transition metal elements and the compounds that they form.

3.1 TRENDS ACROSS PERIOD 3

The period 3 elements are sodium, magnesium, aluminium, silicon, phosphorus, sulfur, chlorine and argon. In chapter 3 of *Chemistry: For use with the IB Diploma Programme Standard Level*, you studied the physical and chemical properties of these elements and found that there was a progression from metallic elements on the left-hand side of the periodic table to non-metallic elements on the right-hand side. The trends in the physical properties of electronegativity, first ionization energy, atomic and ionic radii, and melting and boiling points of these elements were also studied. When considering the oxides of the period 3 elements, their acidic properties were found to vary from basic for the metallic oxides to acidic for the non-metallic oxides. This acidity is shown when the oxide dissolves in water.

Metallic oxides are basic because when they react with water they produce an alkaline solution:

$$\mathrm{Na_2O\,(s) + H_2O(l) \rightarrow 2NaOH(aq)}$$

$$\mathrm{MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)}$$

Interactive Animation

Reaction of sodium and potassium with water

Non-metallic oxides are acidic because when they react with water they produce an acidic solution.

$$\mathrm{P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)}$$

$$\mathrm{SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)}$$

The oxide of aluminium is amphoteric because it can react with an acid or a base:

$$\mathrm{Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)}$$

$$\mathrm{Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)}$$

Note the difference between the terms *amphoteric* and *amphiprotic*. An amphiprotic substance can behave as a Brønsted–Lowry acid or base by donating or accepting a hydrogen ion, H^+, whereas an amphoteric substance can react with an acid or a base, not necessarily by donating or accepting a hydrogen ion.

AS 13.1.1
Explain the physical states (under standard conditions) and electrical conductivity (in the molten state) of the chlorides and oxides of the elements in period 3 in terms of their bonding and structure.
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The chlorides and oxides of period 3 elements

The bonding and structure of the chlorides and oxides of the period 3 elements can be used to explain the physical states of these compounds. As the strength of the bond between the ions in an ionic lattice or between the covalent molecules increases, the melting point increases.

TABLE 3.1.1 PHYSICAL STATES OF PERIOD 3 CHLORIDES UNDER STANDARD CONDITIONS

Group	1	2	3	4	5	6	7
Compound	$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_5	SCl_2	Cl_2
Bonding	Ionic lattice	Ionic lattice	Ionic layer lattice	Covalent molecular	Covalent molecular	Covalent molecular	Covalent molecular
Melting point (°C)	801	714	178 (sublimes)	–70	179	–121	–101
Physical state	Solid	Solid	Solid	Liquid	Solid	liquid	gas

TABLE 3.1.2 PHYSICAL STATES OF PERIOD 3 OXIDES UNDER STANDARD CONDITIONS

Group	1	2	3	4	5	6	7
Highest oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
Bonding	Ionic lattice	Ionic lattice	Ionic lattice	Covalent network lattice	Covalent molecular	Covalent molecular	Covalent molecular
Melting point (°C)	1275	2852	2054	1610	24	17	–92
Physical state	Solid	Solid	Solid	Solid	Solid	liquid	Liquid
Other oxide					P_4O_6	SO_2	Cl_2O
Bonding					Covalent molecular	Covalent molecular	Covalent molecular
Physical state					Liquid	Gas	Gas

Figure 3.1.1 The chlorides of period 3 elements: $NaCl$, $MgCl_2$, Al_2Cl_6, $SiCl_4$, PCl_3 and PCl_5.

Sodium and magnesium oxides and chlorides exhibit ionic bonding. The strong electrostatic attraction between the metal and non-metal ions in three dimensions results in high melting and boiling points. As a result, these compounds are solids under **standard conditions**.

When these compounds are melted, the positive metal ions and negative oxide or chloride ions are free to move. When a potential difference is applied, they can conduct electricity well. The ionic compound is an electrolyte and the result is the decomposition of the compound by electrolysis into its constituent elements.

The structure of aluminium chloride is that of an ionic layer lattice. Under standard conditions of pressure it sublimes at 178°C; however, under conditions of reduced pressure it will melt at 192.5°C. This is a much lower melting point than the other metallic chlorides.

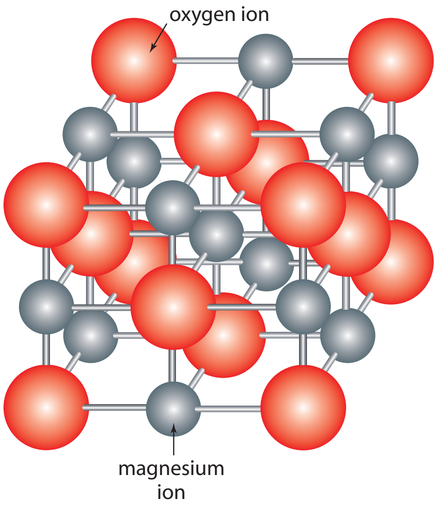

Figure 3.1.2 Magnesium oxide has a lattice structure that is the same as that of sodium chloride.

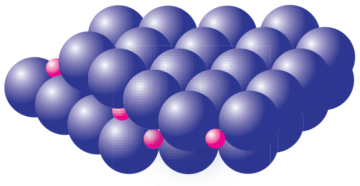

Figure 3.1.3 Solid aluminium chloride has an ionic layer lattice structure.

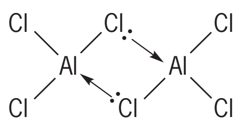

Figure 3.1.4 In the liquid state aluminium chloride exists as a dimer made up of two $AlCl_3$ molecules joined by two dative covalent bonds. This molecular structure means that it does not conduct electricity.

The structure of the compound changes dramatically after melting, and it actually exists as covalently bonded molecules in the liquid and gaseous state. The $AlCl_3$ molecules form dimers in the liquid state. Two dative covalent bonds are formed when a non-bonding electron pair on a chlorine atom of one $AlCl_3$ molecule is shared with the aluminium atom of the second $AlCl_3$ molecule in the dimer. At high temperatures the dimers dissociate, existing as individual trigonal planar $AlCl_3$ molecules in the gaseous state.

Under standard conditions aluminium chloride will not melt; however, at reduced pressures it does melt and the electrical conductivity is observed to rise to a value that is quite high just before the melting point is reached. When molten, however, $AlCl_3$ does not conduct electricity at all. This can be attributed to its covalent molecular structure.

Aluminium oxide, Al_2O_3, has a very high melting point that is clearly the result of ionic bonding between the Al^{3+} ions and the O^{2-} ions. Aluminium oxide, also known as alumina, is a powdery white solid. In its crystalline form it is called corundum (see Chem Complement). Molten aluminium oxide conducts electricity well. It is this property that allows molten alumina to be electrolysed to produce aluminium metal.

CHEM COMPLEMENT

What does sandpaper have in common with rubies and sapphires?

Figure 3.1.5 Sapphire is a form of corundum, Al_2O_3. These sapphires were separated from river gravel by panning.

Corundum is a crystalline form of aluminium oxide, Al_2O_3. It is very dense and very hard—it is the second hardest material after diamond. Most corundum occurs as white, grey, dull blue or dull red crystals. However, a very small amount of corundum has a transparency, purity and colour that make it suitable for use as a gemstone. These gemstones can have a range of colours. Red corundum is called ruby, blue corundum is called sapphire, and other colours usually are named with the colour specified as a prefix to the word sapphire, for example, green sapphire. A rare variety is the orange sapphire that is also called padparascha.

The colours of the corundum gems are caused by small amounts of metal oxide impurities. Chromic oxide, Cr_2O_3, causes brilliant red colouring in corundum, thereby producing rubies. Ferric oxide, Fe_2O_3, causes yellow colouration, titanium(IV) oxide, TiO_2, produces vivid blue. Titanium oxide also causes an effect called asterism, in which a star-like formation of concentrated light can be seen in the gem.

Non-gem quality samples of corundum can be used as an abrasive in industry and are embedded in sandpaper.

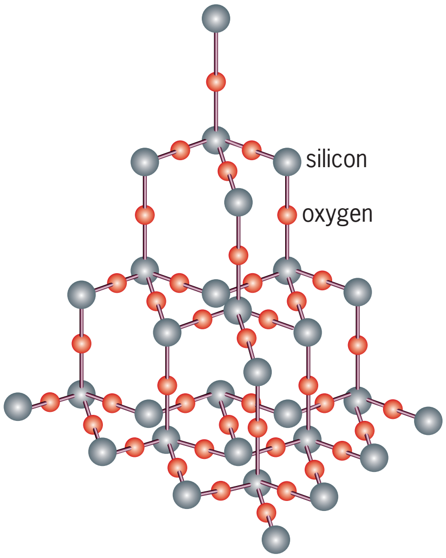

Figure 3.1.6 Silicon dioxide exists in a giant covalent network lattice structure.

The structure of silicon dioxide, SiO_2, is that of a giant covalent network lattice. Every bond within that structure is a single covalent bond in which a pair of electrons is shared between two atoms. The great strength of these bonds means that silicon dioxide has a very high melting point and so is a solid under standard conditions. In comparison, silicon chloride, $SiCl_4$ exists as discrete covalent molecules with weak van der Waals' forces between the molecules. It is a liquid under standard conditions.

The molecules of silicon chloride are non-polar. Silicon chloride does not conduct electricity in its liquid state due to the absence of charged particles (ions or electrons) that are free to move. Similarly, in the liquid state silicon dioxide is a very poor conductor of electricity. The coating of silicon dioxide that occurs naturally on the surface of silicon is valued for its properties as an electrical insulator.

Phosphorus chlorides are covalent in nature. Phosphorus(III) chloride, PCl_3, and phosphorus(V) chloride, PCl_5, are both important chlorides of phosphorus. Their molecular shapes are trigonal pyramidal and trigonal bipyramidal respectively. Phosphorus(III) chloride is slightly polar, so dipole-dipole attractive forces and van der Waal's forces exist between the covalently bonded molecules. Phosphorus(V) chloride is non-polar with only van der Waals' forces between its molecules. It has a higher melting point than phosphorus(III) chloride because of the greater strength of the van der Waals' forces between the larger PCl_5 molecules. As a result, phosphorus(V) chloride is a solid and phosphorus(III) chloride is a liquid under standard conditions (see figure 3.1.1).

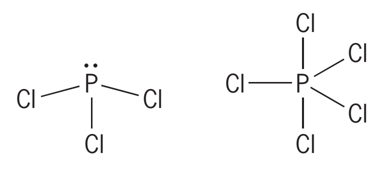

Figure 3.1.7 Phosphorus(III) chloride is a trigonal pyramidal molecule and phosphorus(V) chloride is a trigonal bipyramidal molecule.

There are two oxides of phosphorus, P_4O_6 and P_4O_{10}. The molecules are held together by weak van der Waals' forces in the solid state, with those of P_4O_{10}, a white powder, being stronger than those of P_4O_6, a white waxy solid, due to the larger size of the P_4O_{10} molecule.

The phosphorus chlorides and oxides are covalently bonded molecular substances and so do not conduct electricity in the liquid state, as there are no charged particles that are free to move.

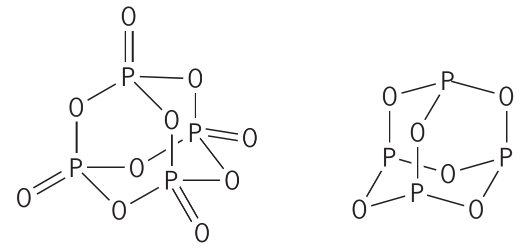

Figure 3.1.8 The structures of phosphorus(V) oxide, P_4O_{10} and phosphorus(III) oxide, P_4O_6.

Sulfur dioxide is a gas under standard conditions and sulfur trioxide is a liquid. Both are molecular in nature and do not conduct electricity in the liquid state, since the molecules do not carry an overall charge. (There are no free-moving charged particles.) Sulfur dichloride, SCl_2, is a molecular substance that is a liquid under standard conditions. Like sulfur trioxide it does not conduct electricity.

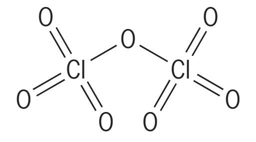

Figure 3.1.9 Dichlorine heptoxide is an explosive compound whose molecules are V-shaped.

Chlorine forms a number of oxides that have a tendency to explode. Dichlorine oxide, Cl_2O, is a strongly oxidizing orange gas that can easily be ignited. Dichlorine heptoxide, Cl_2O_7, is an unstable, molecular liquid with weak van der Waals' forces between the molecules. Chlorine dioxide, ClO_2, is a yellow gas that is used in the paper-making industry to bleach wood pulp.

Chlorine gas, Cl_2, exists as non-polar molecules with very weak van der Waals' forces between the molecules. Its boiling point is –34°C.

As molecules in the liquid state, neither the oxides of chlorine nor chlorine itself conduct electricity.

Argon does not form chlorides or oxides due to its complete valence shell of electrons.

The reactions of chlorine and the chlorides with water

AS 13.1.2 Describe the reactions of chlorine and the chlorides referred to in 13.1.1 with water. © IBO 2007

Sodium and magnesium chlorides are both ionic in nature. Sodium chloride dissolves in water to form a neutral solution, while an aqueous solution of magnesium chloride is slightly acidic.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$

$$MgCl_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2Cl^-(aq)$$

When solid sodium chloride is placed in water, the dissolving process involves the dissociation of the sodium and the chloride ions and the subsequent assimilation of the ions into the solution. The sodium ions and the chloride ions are surrounded by water molecules and become part of the solution.

QuickTime CW Video NaCl in water

The polar water molecules are attracted to the ions by ion–dipole bonding. Each sodium ion is surrounded by water molecules, with the slightly negative oxygen part of the molecule facing the positive sodium ion; each chloride ion is surrounded by water molecules, with the slightly positive hydrogen part of the molecule facing the negative chloride ion.

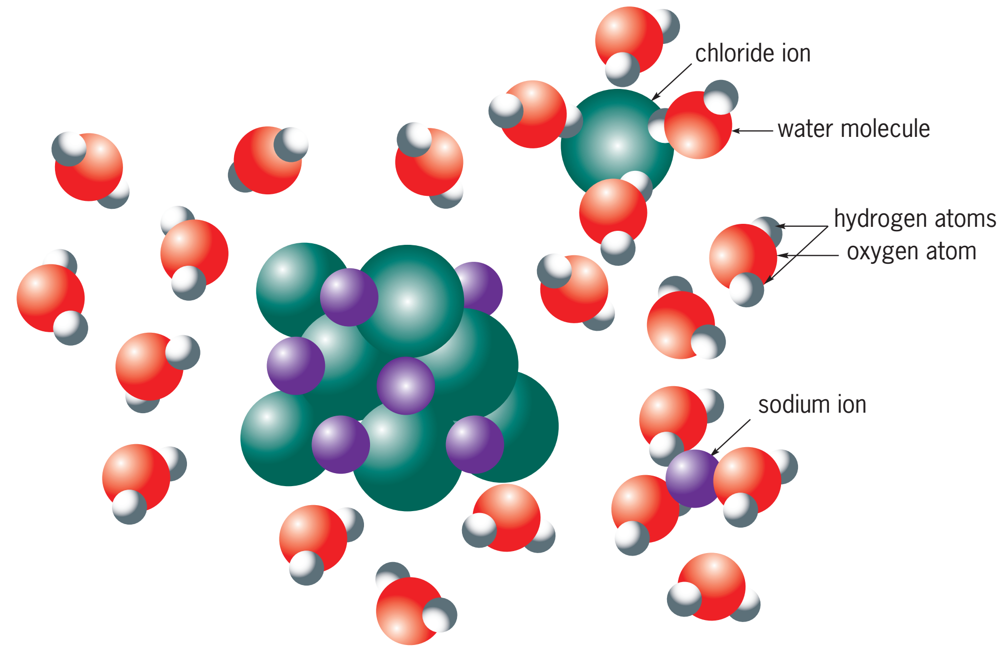

Figure 3.1.10 When sodium chloride dissolves in water, the sodium ions and chloride ions are surrounded by the polar water molecules.

Magnesium chloride behaves in a similar manner in water, although the greater charge on the smaller magnesium ion allows dative (coordinate) bonds to form between the Mg^{2+} ion and the surrounding water molecules. This results in the formation of hexaaquamagnesium ions, $[Mg(H_2O)_6]^{2+}$, which are able to donate a hydrogen ion, resulting in the slightly acidic (pH = 6) nature of this solution.

$$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$$

When anhydrous aluminium chloride reacts with a small amount of water, the mixture spits vigorously and hydrogen chloride gas is given off as acidic fumes. The reaction that occurs can be represented as:

$$AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)$$

With a slight excess of water, this reaction produces a highly acidic solution. This manner of reacting is typical of covalent chlorides.

Aluminium chloride acts as both a Lewis acid and a Brønsted–Lowry acid (see section 7.5 p. 228). When added to a large amount of water, aluminium chloride dissolves, producing an acidic solution with a pH as low as 3. The Lewis acidity of the aluminium chloride solution can be attributed to the small size and high charge of the Al^{3+} ion.

$$AlCl_3(s) \xrightarrow{aq} [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$$

The water molecules surrounding the aluminium ion are attached through dative (coordinate) covalent bonds, so the aluminium ion is an electron pair acceptor, a Lewis acid. The water molecules become even more strongly polarized than usual, and the hydrogen atoms are so weakly bonded to the oxygen atoms that they can be donated as H^+ ions to surrounding water molecules.

$$\underset{\text{acid}}{[Al(H_2O)_6]^{3+}(aq)} + \underset{\text{base}}{H_2O(l)} \rightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

In this reaction the **hydrated** aluminium ion is acting as a Brønsted–Lowry acid.

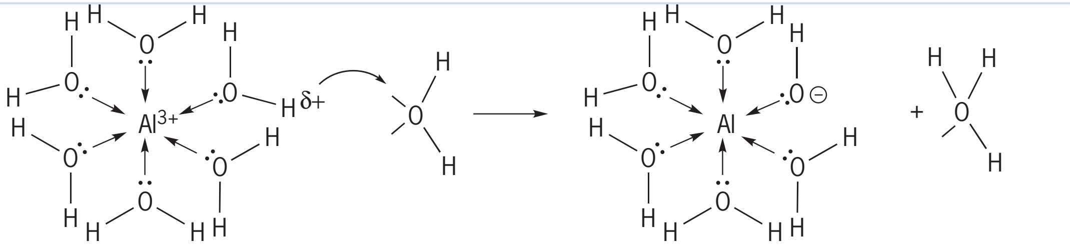

Figure 3.1.11 $[Al(H_2O)_6]^{3+}$ reacts with water to produce an acidic solution.

As they are covalent chlorides, $SiCl_4$, PCl_3 and PCl_5 react with water—they are hydrolysed. The hydrogen chloride dissolves in water to form a highly acidic solution with a pH value close to zero.

$$SiCl_4(l) + 2H_2O(l) \rightarrow 4HCl(g) + SiO_2(s)$$

$$PCl_3(l) + H_2O(l) \rightarrow HCl(g) + H_3PO_3(aq)$$

$$PCl_5(s) + 4H_2O(l) \rightarrow 5HCl(g) + H_3PO_4(aq)$$

Chlorine gas, Cl_2, dissolves in water to make a solution that is known as chlorine water. Like the other covalent chlorides, it reacts with water. In this case a mixture of hypochlorous acid, HOCl, and hydrochloric acid, HCl is produced.

$$Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + HCl(aq)$$

The formation of the hypochlorite ion, OCl^-, is primarily responsible for the widespread application of chlorine as a disinfectant for water.

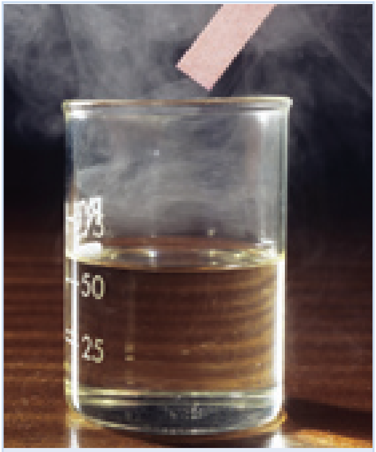

Figure 3.1.12 Silicon(IV) chloride, $SiCl_4$, even reacts with water vapour in the air, producing an acidic vapour that turns blue litmus paper pink.

CHEM COMPLEMENT

Making your swimming pool safe

Figure 3.1.13 Chlorine is used to disinfect water to make it safe for public swimming.

A pleasant pastime on a hot summer's day is to take a swim in a cool, clear swimming pool. Unfortunately, still water provides a home to many algae and bacteria that would make us sick if we didn't add chemicals to our private and public swimming pools. Many of the compounds added to keep swimming pools clear and clean contain chlorine, although the more expensive bromine-containing compounds may be used for spas.

In a large public swimming pool, chlorine gas, Cl_2, may be used. It reacts with the water to produce hypochlorous acid, HOCl, a powerful killer of bacteria and algae.

$$Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + HCl(aq)$$

In low concentrations hypochlorous acid does not bother most people. Compounds containing hypochlorite ions (also an effective killer of bacteria) are used in home swimming pools. These include calcium hypochlorite, $Ca(OCl)_2$, lithium hypochlorite, LiOCl, and sodium hypochlorite, NaOCl, and are supplied as solid tablets of the compound (known as 'dry chlorine') or as aqueous solutions (known as 'liquid chlorine').

The power of the hypochlorite ion as an oxidizing agent is also used in swimming pool chemistry when it is added to remove chloramines that form when chlorine reacts with ammonia and nitrogen compounds (e.g. urine) in the water. Chloramines cause an unpleasant chlorine odour and eye irritation to swimmers.

THEORY OF KNOWLEDGE

As part of your internally assessed experimental work you will design and carry out experiments to confirm the theories and laws studied in class. One person who thought it was strange to design experiments in order to confirm the effects of an already known theory or law was the Austrian science philosopher Karl Popper (1902–1994). For example, the periodic law states that the elements when arranged in the order of atomic number show periodic variation in their chemical and physical properties. If this law was tested over and over again, under controlled conditions, it would be confirmed each time. Popper believed that scientists should not focus on finding conditions where a law is confirmed but on finding a way to prove it false. He believed 'falsifying' a law would enable more creative thinking and would allow scientists to test new ideas by trial and error rather than just confirming patterns they already knew.

Popper's philosophy, however, did not find favour with all scientists. In fact many important discoveries have occurred because scientists refused to abandon experimental work when the results obtained did not match the original hypothesis. Remember that Mendeleev refused to reject his periodic law hypothesis even when his results showed repeatedly there was no periodic variation. It was only later after much perseverance that he realized that this contradictory evidence was due to experimental error, and not his hypothesis.

- Imagine you were carrying out an experiment to confirm the reactions of chlorine and the third period chlorides with water and your results contradicted your hypothesis. What would you do?
- How could you disprove the hypothesis that all compounds made from metal and non-metal elements are ionic?

Section 3.1 Exercises

1 Compare the bonding and structure of NaCl with that of PCl_3.

2 Considering their structure and bonding, explain why molten Na_2O conducts electricity whereas liquid SO_3 does not.

3 Describe the bonding in P_4O_{10} and hence explain why it does not conduct electricity.

4 Describe the processes that occur when a sample of solid sodium chloride is placed in water.

5 Describe the processes that occur when a sample of phosphorus(V) chloride is placed in water.

6 Considering your answers to questions **4** and **5**, explain why a difference is seen between the reactivity of NaCl and PCl_5 with water.

7 Explain, using chemical equations, why a solution of aluminium chloride is acidic.

8 Write equations for the reactions of each of the following chlorides with water.

- **a** chlorine, Cl_2
- **b** silicon chloride, $SiCl_4$
- **c** magnesium chloride, $MgCl_2$

3.2 FIRST ROW d-BLOCK ELEMENTS

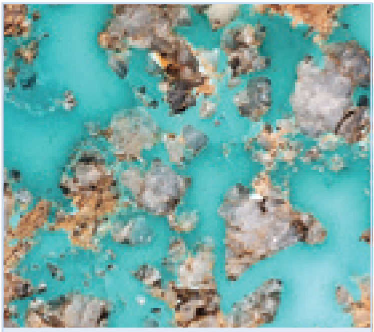

Figure 3.2.1 Turquoise is a rare opaque mineral that is a hydrated copper aluminium phosphate.

Between groups 2 and 3 in the periodic table are found the **d-block elements**, which include some of the most widely used elements in everyday life. These d-block elements have played an important role in different cultural traditions over thousands of years. Iron was one of the first metals extracted from its ore and made into tools. The semiprecious stone turquoise contains the element copper and has been valued for thousands of years in the Middle East and Asia for its beauty. When bronze, a mixture of copper and tin, was discovered in ancient Egypt, it marked the end of the Iron Age and the start of the Bronze Age. The properties and uses of everyday materials were revolutionized. The Bronze Age in China started in the 21st century BC and lasted about 2000 years. Bronze was used to make precious metalware (vessels to hold food, wine and water). It was also used in important ceremonies and to make musical instruments and armoury. Bronze was valued for its strength, durability and the 'golden' colour imparted to it by the presence of copper in the mixture. Early Chinese ceramics and pottery were made from iron-rich clays. The elements cobalt, iron, copper and manganese were used to create the beautiful coloured glazes on the pottery.

AS **13.2.1**
List the characteristic properties of transition elements.
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You will recall from chapter 1 that in the d-block elements, electrons are being added to the d subshell of the third and subsequent shells. The first row of d-block elements consists of those elements whose highest energy electrons are filling the 3d subshell. These elements are scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc. Of these, the elements titanium to copper are considered to be **transition elements**. This distinction is due to the definition of a transition element as a d-block element that can form at least one stable ion with a *partially filled* d subshell.

CHEM COMPLEMENT

Manganese in your diet

Manganese is an essential trace element found in the human body. Most humans have about 10–20 mg in their bodies. Most of this is concentrated in the pancreas, bone, liver and kidneys.

Manganese has various functions within the human body, including strengthening of cell membranes to help protect against viruses and other infections. It is an enzyme activator that helps to create fatty acids and cholesterol, as well as glycogen. It helps to strengthen bones, collagen and connective tissue such as ligaments. It also helps to promote normal nerve function, and it plays a part in sexual function and in producing breast milk. Sources of manganese in the diet include raspberries, pineapple, brown rice, soybeans and spinach.

Figure 3.2.2 Raspberries are a source of manganese in our diet. It has been suggested that a diet high in berries is useful in reducing susceptibility to cancerous growths.

AS 13.2.2
Explain why Sc and Zn are not considered to be transition elements.
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If we consider the electron configurations of these d-block elements and the ions that they can form, we can see clearly why scandium and zinc are not included as transition metals. Recall from chapter 1 that when ions of first row d-block elements are formed electrons are first lost from the 4s subshell before the 3d subshell.

TABLE 3.2.1 **ELECTRON CONFIGURATIONS OF d-BLOCK ELEMENTS AND ONE ION**

Element	Atomic number (Z)	Electron configuration of element	One ion of the element	Electron configuration of ion	Presence of partially filled d subshell
Scandium	21	$[Ar]3d^1 4s^2$	Sc^{3+}	$[Ar]$	No
Titanium	22	$[Ar]3d^2 4s^2$	Ti^{2+}	$[Ar]3d^2$	Yes
Vanadium	23	$[Ar]3d^3 4s^2$	V^{2+}	$[Ar]3d^3$	Yes
Chromium	24	$[Ar]3d^5 4s^1$	Cr^{2+}	$[Ar]3d^4$	Yes
Manganese	25	$[Ar]3d^5 4s^2$	Mn^{2+}	$[Ar]3d^5$	Yes
Iron	26	$[Ar]3d^6 4s^2$	Fe^{2+}	$[Ar]3d^6$	Yes
Cobalt	27	$[Ar]3d^7 4s^2$	Co^{2+}	$[Ar]3d^7$	Yes
Nickel	28	$[Ar]3d^8 4s^2$	Ni^{2+}	$[Ar]3d^8$	Yes
Copper	29	$[Ar]3d^{10} 4s^1$	Cu^{2+}	$[Ar]3d^9$	Yes
Zinc	30	$[Ar]3d^{10} 4s^2$	Zn^{2+}	$[Ar]3d^{10}$	No

In table 3.2.1, one ion has been selected to demonstrate the presence of a partially filled d subshell. In the case of scandium and zinc, only one ion exists and that ion does not have a partially filled d subshell. The scandium(III) ion, Sc^{3+}, is the only stable ion of scandium and has no electrons in the 3d subshell. The zinc(II), Zn^{2+}, ion is the only stable ion of zinc to exist and this ion has a full 3d subshell. Notice that all transition elements can show an oxidation number of +2.

In examining the d-block elements thus far, we have touched on one characteristic property of transition elements—their ions can exist in variable oxidation states.

In addition to this property, there are a number of other characteristic properties of transition elements:

- They have higher melting points and are harder and denser than group 1 and 2 metals.
- A number of the elements and their compounds have catalytic properties.
- They can form complex ions (see section 3.3).
- The majority of their compounds are coloured (see section 3.3).

Variable oxidation states

13.2.3
Explain the existence of variable oxidation number in ions of transition elements.© IBO 2007

Transition elements can form ions with a variety of oxidation states (oxidation numbers). All transition elements can form ions with an oxidation number of +2, and, in addition, each element can form a number of ions with other oxidation numbers. From titanium to manganese, the maximum oxidation number possible is equal to the total number of 4s and 3d electrons. For example, the maximum oxidation number possible for titanium ([Ar]$3d^2 4s^2$) is +4 and for manganese ([Ar]$3d^5 4s^2$) it is +7.

Demonstration 3.1
Oxidation states of vanadium and manganese

TABLE 3.2.2 **SOME COMMON OXIDATION STATES FOR THE TRANSITION ELEMENTS AND COMPOUNDS IN WHICH THESE OXIDATION STATES OCCUR**

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
							+1 Cu_2O
+2 $TiCl_2$	+2 VCl_2	+2 $CrCl_2$	+2 $MnCl_2$	+2 $FeSO_4$	+2 $CoCl_2$	+2 $NiSO_4$	+2 $CuSO_4$
+3 $TiCl_3$	+3 VCl_3	+3 $CrCl_3$	+3 $Mn(OH)_3$	+3 Fe_2O_3			
+4 TiO_2	+4 VO_2	+6 $K_2Cr_2O_7$	+4 MnO_2				
	+5 V_2O_5		+7 $KMnO_4$				

The transition elements form ions by losing electrons from both the 4s and the 3d subshells. This is possible because these subshells are very close to each other in energy. You will recall that the 4s subshell is filled before the 3d subshell because an empty 4s subshell is lower in energy than the 3d subshell; however, when full, electrons are removed from the 4s subshell before 3d. For this interchange to occur, the energy of the two subshells must be very close, indeed.

Interactive Animation
Oxidation states of transition metals

QuickTime Video
Common oxidation states

Figure 3.2.3 Manganese can be found in a range of oxidation states including (a) manganese(III) and (b) manganese(VII).

The variation in oxidation states is easily recognizable in many transition elements by a change in colour of the new compound. This can be used in redox titrations, removing the need for an indicator, and is useful in the oxidation of organic compounds such as alcohols, where the product and reactant are both colourless, but the colour change in the oxidising agent (e.g. $Cr_2O_7^{2-}$) indicates that the reaction has occurred.

$$\mathbf{Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)}$$

(See *Chemistry: For use with the IB Diploma Programme Standard Level*, chapter 10 for half-equations of redox reactions, p. 310, and chapter 11 for oxidation of alcohols, p. 392.)

Figure 3.2.4 When ethanol is oxidized by potassium dichromate, the orange $Cr_2O_7^{2-}$ ion is reduced to the dark green Cr^{3+} ion.

Physical properties

The d-block elements are all metals. They have physical properties that are typical of metals. With the exception of mercury, which is a liquid at room temperature, their melting points are high and they are solids under standard conditions. They are good conductors of electricity and heat, and are hard, strong and shiny.

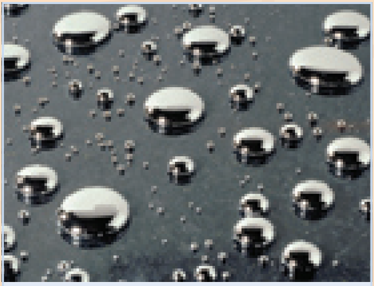

Figure 3.2.5 Mercury is a liquid under standard conditions.

TABLE 3.2.3 MELTING POINTS AND DENSITIES OF SOME METALS

Element	Group	Melting point (°C)	Density (g cm^{-3})
Sodium	1	98	0.97
Potassium	1	64	0.86
Magnesium	2	649	1.74
Titanium	d-block	1660	4.54
Chromium	d-block	1857	7.15
Iron	d-block	1535	7.87

The chemical reactivity of d-block elements is relatively low and, together with these physical properties, makes d-block elements extremely useful. Iron is used widely for construction of bridges, buildings, vehicles and other structures that require great strength. Copper is most valuable for its excellent conduction of electricity and as a unreactive, yet malleable, metal for water pipes. Chromium is used for plating less-attractive metals while maintaining their strength; and titanium is light, strong and corrosion resistant—making it an excellent material for jet engine parts.

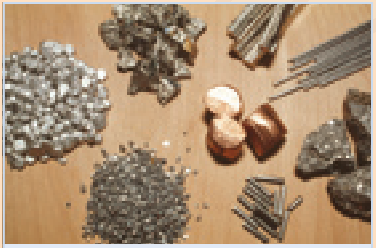

Figure 3.2.6 A variety of transition elements including copper, nickel, titanium and chromium.

Catalytic properties

A catalyst increases the rate of a chemical reaction by providing an alternate reaction pathway with a lower activation energy. The catalyst itself is not consumed. As the activation energy is lowered, there will be a greater proportion of particles present at a given temperature with sufficient kinetic energy to overcome the activation energy.

Many transition metals and their compounds show catalytic activity and they are widely used in industry, where it is desirable to generate maximum quantities of product as quickly as possible to maximize profits. Indeed, there are many industrial processes that would simply not be viable without the use of catalysts, and a great deal of research is undertaken by industries to find the most effective and cheapest catalyst for the production of particular substances.

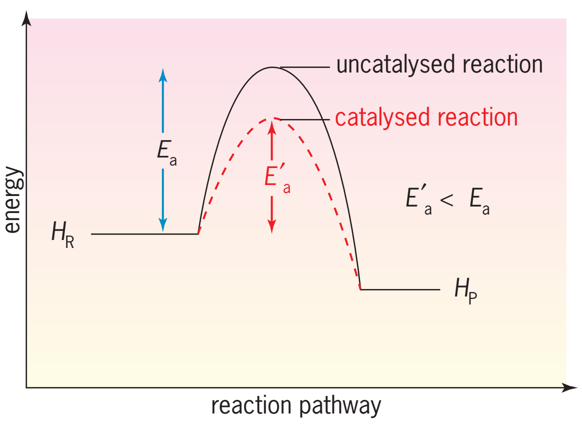

Figure 3.2.7 Catalysts lower the activation energy (E_a) and so increase the rate of reaction.

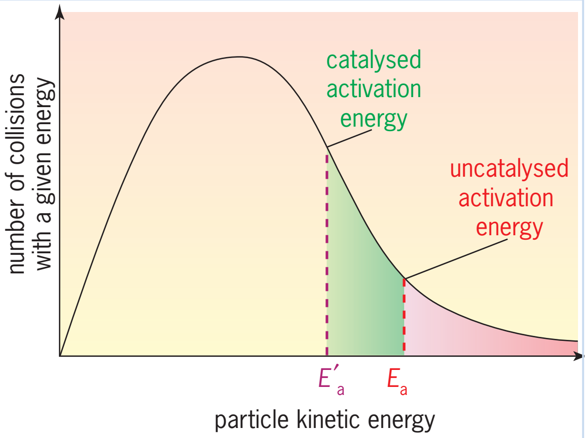

Figure 3.2.8 A catalyst lowers the activation energy (E_a) so that a greater proportion of collisions will result in product formation.

13.2.7 State examples of the catalytic action of transition elements and their compounds. © IBO 2007

Worksheet 3.1
The role of catalysts

TABLE 3.2.4 INDUSTRIAL CATALYSTS

Process	Catalyst
Decomposition of NO in catalytic converter of car exhausts	Platinum–rhodium alloy
Hydrogenation of alkanes	Alloy of nickel and aluminium
Decomposition of H_2O_2	Manganese(IV) oxide, MnO_2
Haber process to make NH_3	Porous iron (can use osmium)
Contact process to make H_2SO_4	Vanadium(V) oxide pellets

Solid catalysts generally have a high surface energy, where this term refers to the amount of energy required to create a new surface. Due to their high surface energies, solid catalysts are able to form strong bonds with the molecules that come into contact with them; we say the reactant molecule adsorbs (sticks) onto the surface. This attraction at the surface of the catalyst weakens the bonds within the reactant molecules, making it easier to break them apart. Collisions with other molecules are now more likely to overcome the activation energy for the reaction, and so the rate of product formation is increased.

Figure 3.2.9 A variety of catalytic converters are used in car exhaust systems.

Nickel is used as a catalyst in the hydrogenation of alkenes to form alkanes. A practical application of this process is in the manufacture of margarine. The vegetable oils used for making margarines are refined as liquids that are high in unsaturated fatty acids. To increase the melting point of the mixture, the fatty acids undergo hydrogenation during which some carbon–carbon double bonds are converted to single bonds and hydrogen is added. This process is similar to the hydrogenation of ethene to form ethane:

$$H_2C=CH_2 + H_2 \xrightarrow{Ni} H_3C{-}CH_3$$

Platinum, rhodium and palladium are particularly effective, though very expensive, industrial catalysts. Metal **alloys** (mixtures of the metal with one or more other elements) made from such elements are often plated in a very thin layer over a honeycombed surface of an inert material such as aluminium or silica. By maximising the surface area of the catalyst, the amount of reactant that can adsorb onto the surface is increased, enhancing the effectiveness of the catalyst. Alloys of platinum and rhodium are used in the catalytic converters of car exhaust systems, where toxic gaseous emissions such as CO, NO and NO_2 are broken down into harmless compounds.

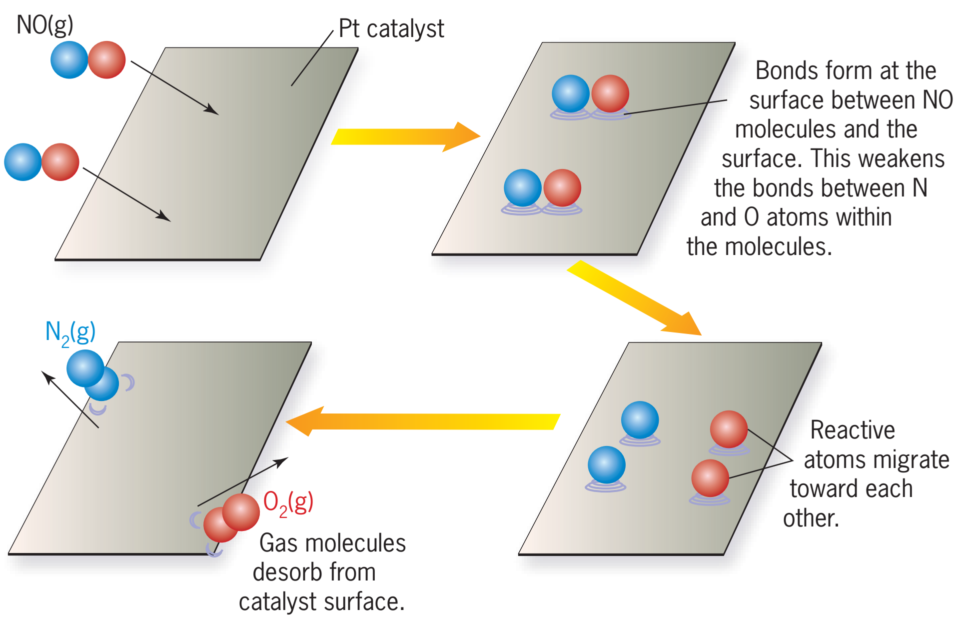

Figure 3.2.10 Molecules of NO adsorb onto the surface of a platinum catalyst in a catalytic converter and are broken down to N_2 and O_2.

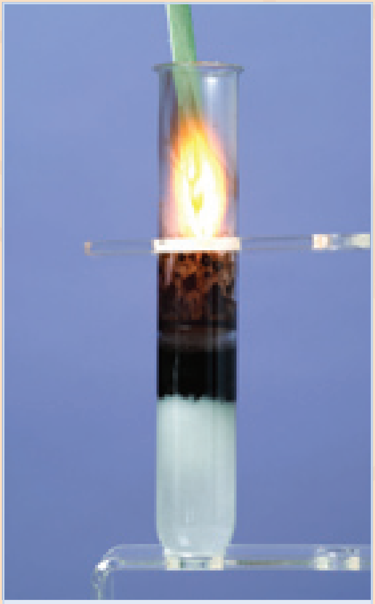

Figure 3.2.11 The decomposition of hydrogen peroxide can be catalysed by the black powder, MnO_2. The rate at which oxygen is released is dramatically increased and easily re-lights a glowing splint.

Living systems rely heavily on catalysts for the swift and orderly progress of chemical reactions within cells. Biological catalysts are better known as enzymes, and it is estimated that the human body utilizes more than 100 000 different enzymes, many of which contain transition metal ions. Cobalt, Co, in vitamin B_{12} is an example. Vitamin B_{12} is essential for the production of red blood cells and for the correct functioning of the central nervous system. Cobalt atoms bond to different parts of the vitamin B_{12} structure.

Hydrogen peroxide is a toxin in the human body. Its decomposition is catalysed by the enzyme catalase. In the laboratory the decomposition of hydrogen peroxide can be catalysed by a number of inorganic catalysts, among them manganese(IV) oxide, MnO_2.

$$2H_2O_2(l) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

Another example of a transition element contributing to essential processes in the human body is the presence of Fe^{2+} ions as a central part of the heme group of hemoglobin. Hemoglobin is the oxygen-carrying protein attached to red blood cells. A lack of hemoglobin results in anemia due to a lack of oxygen reaching the cells of the body.

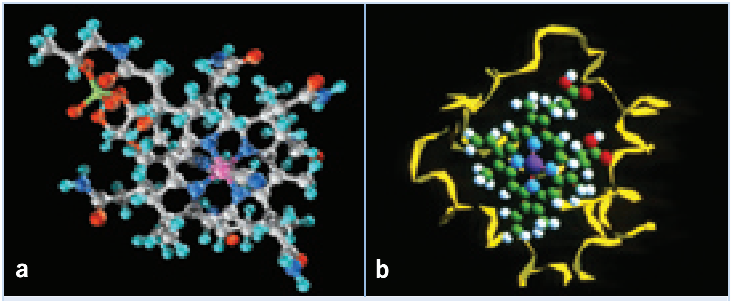

Figure 3.2.12 (a) Cobalt (pink sphere) is an important part of the structure of vitamin B_{12} and (b) iron (purple sphere) is central to the heme group in the oxygen-carrying hemoglobin protein.

Catalysts are often grouped according to their phase in comparison to the reactions with which they are involved. **Homogeneous catalysts** are in the same phase as the reactants and products, for example in the aqueous state when reactants and products are also aqueous.

Heterogeneous catalysts are in a different state to the reactants. Many of the important industrial processes making chemicals such as sulfuric acid and ammonia rely on heterogeneous catalysts to overcome the disadvantage of having to use lower than ideal temperatures in order to produce satisfactory yields at equilibrium.

AS 13.2.8 Outline the economic significance of catalysts in the Contact and Haber processes. © IBO 2007

In catalysis, the oxidation state of the transition element may change during the reaction, but it is regenerated at the end of the reaction. An example of this is found in the Contact process for making sulfuric acid. During the Contact process sulfur dioxide, SO_2, is oxidized to sulfur trioxide, SO_3, and a solid catalyst of pellets of vanadium(V) oxide (V_2O_5) is employed:

$$2SO_2(g) + O_2(g) \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3(g) \quad \Delta H = -197 \text{ kJ mol}^{-1}$$

As discussed in chapter 8 of *Chemistry: For Use with the IB Diploma Programme Standard Level*, this equilibrium is an exothermic reaction, and so is favoured by low temperatures and high pressures. At low temperatures, however, the reaction proceeds slowly, so a catalyst is used to improve the rate of reaction and the economic viability of the Contact process. The vanadium(V) oxide, V_2O_5, is laid out in a series of three or four trays in pellet form. By using trays of pellets, the surface area of the catalyst is increased, and so is its effectiveness. The vanadium(V) oxide is an oxidizing agent and oxidizes the sulfur dioxide to sulfur trioxide, itself being reduced to vanadium(IV) oxide. The vanadium(IV) oxide is then oxidized by oxygen to reform vanadium(V) oxide.

$$SO_2(g) + V_2O_5(s) \rightarrow SO_3(g) + 2VO_2(s)$$

$$4VO_2(s) + O_2(g) \rightarrow 2V_2O_5(s)$$

Similarly, in the Haber process, for the production of ammonia, a porous form of iron (with potassium hydroxide added to it) is used as a catalyst for the reaction:

$$N_2(g) + 3H_2(g) \overset{Fe}{\rightleftharpoons} 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

This catalyst is cheaper than other transition elements such as osmium, which also catalyse the reaction. Without a catalyst, this reaction is very slow and not economically viable.

CHEM COMPLEMENT

The Ostwald process

An example of a solid catalyst in action is seen in the Ostwald process. In 1901 the German chemist Wilhelm Ostwald (1853–1932) invented a process for converting industrial quantities of ammonia into nitric acid. Nitric acid (HNO_3) is an important raw material in the manufacture of fertilizers, explosives, drugs and dyes. In the first stage of this process, ammonia is oxidized to nitrogen monoxide in the presence of a platinum–rhodium catalyst:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$$

In order to maximize the effective surface area of the catalyst, a wire mesh made of the alloy is woven into a flexible sheet through which the reactant gases are passed. The wire mesh catalyst may remain functional for up to 6 months; however, it is expensive. At a cost of about twice that of gold for the alloy, a single circular sheet of catalyst mesh with a diameter of up to 5.5 m costs well in excess of US$1 million!

At high temperatures, the oxidation of ammonia in air produces nitrogen gas rather than NO, which is why a catalyst must be employed, and reaction conditions carefully regulated to ensure that the preferred reaction takes place. The wire gauze is electrically heated and the reactant gas mixture is passed across it very quickly, with a contact time of only 3 milliseconds. This swift passage prevents the nitrogen monoxide from decomposing to N_2 and O_2 and consequently being lost. Ostwald was awarded the Nobel Prize in Chemistry in 1909 for his work on catalysts and chemical equilibria.

Figure 3.2.13 A platinum–rhodium alloy gauze is used as a catalyst in the manufacture of nitric acid.

Section 3.2 Exercises

1 Write the expected electron configuration for:

- **a** Cr^{3+}
- **b** Cu^{+}
- **c** Mn^{4+}
- **d** Co^{3+}

2 Deduce the highest expected oxidation state for each of the following transition elements.

- **a** Ti
- **b** V
- **c** Cr
- **d** Mn
- **e** Fe
- **f** Cu

3 Write the formula for the chloride corresponding to the highest expected oxidation state for:

- **a** Sc
- **b** Co
- **c** Zn

4 Write the formula for the oxide corresponding to the highest expected oxidation state for:

   a Ti

   b Ni

   c Cr

5 Write the half-equation for the conversion of each of the following transition metals to the different oxidation state.

   a Fe^{2+} to Fe^{3+}

   b MnO_4^- to Mn^{2+}

   c VO^{2+} to V^{3+}

6 Describe the role of the platinum–rhodium catalyst in the catalytic converter of a car.

7 In one stage of the industrial production of sulfuric acid, sulfur dioxide gas is oxidized to sulfur trioxide gas in the presence of a catalyst of vanadium(V) oxide. The catalyst is used in pellets and the gaseous mixture is passed over layers, or beds, of catalyst. The equation for this reaction is:

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

   a Why is the vanadium(V) oxide used in pellets rather than as a single mass?

   b Is the V_2O_5 a homogeneous or heterogeneous catalyst in this reaction?

   c What possible advantage could be gained by passing the gas mixture over several beds of catalyst?

3.3 TRANSITION METAL COMPLEXES

Transition metal ions are characteristically small and highly charged. This high charge density results in an ability to strongly attract ions and small polar molecules, forming a **complex ion** in which **coordinate (dative) bonds** link the transition metal ion to the surrounding molecules or ions.

The ions and small polar molecules attracted to the transition metal cation are called ligands. A **ligand** has an electron pair that it can donate to the central metal ion. Typically two to six ligands may surround a transition metal ion in a complex. The number of ligands surrounding the central ion is called the **coordination number**. Common ligands that are neutral molecules include water, H_2O; ammonia, NH_3; and carbon monoxide, CO. These molecules have at least one pair of non-bonding electrons with which they can form a coordinate bond. Negative ions that can be ligands include the chloride ion, Cl^-; hydroxide ion, OH^-; and the cyanide ion, CN^-.

AS 13.2.4
Define the term *ligand.*
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TABLE 3.3.1 NAMES OF SOME LIGANDS

Ligand	Formula	Name
Ammonia	$:NH_3$	Ammine-
Carbon monoxide	$:CO$	Carbonyl-
Chloride ion	$:Cl^-$	Chloro-
Cyanide ion	$:CN^-$	Cyano-
Hydroxide ion	$:OH^-$	Hydroxo-
Water	$H_2O:$	Aqua-

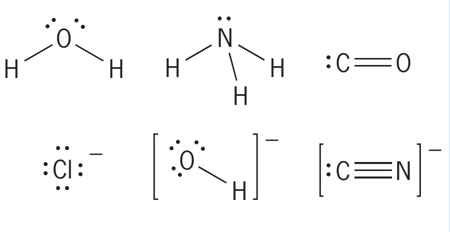

Figure 3.3.1 Ligands have an electron pair that can be donated to a transition metal cation.

AS 13.2.5
Describe and explain the formation of complexes of d-block elements.
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The type and number of ligands surrounding the central metal ion is indicated in the name of the complex. The shape of the complex ion depends on the number of ligands surrounding the cation. These geometrical shapes are the same as those assumed by molecules with 2 to 6 atoms (and no non-bonding electrons) surrounding them.

Formation of transition metal complexes

The atomic radii of the elements whose highest energy electrons are filling the 3d subshell (the first transition series) are all significantly smaller than those of potassium and calcium. Notice in figure 3.3.2 that the ionic radii of the later transition metal ions Fe^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} are all very small. These ions form complexes more easily than Ti^{2+} and V^{2+}.

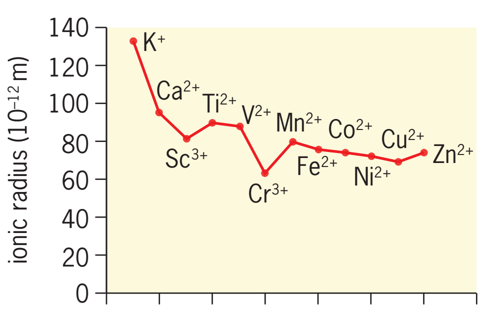


Figure 3.3.2 The ions of the first transition series are significantly smaller than K^+ and Ca^{2+}.

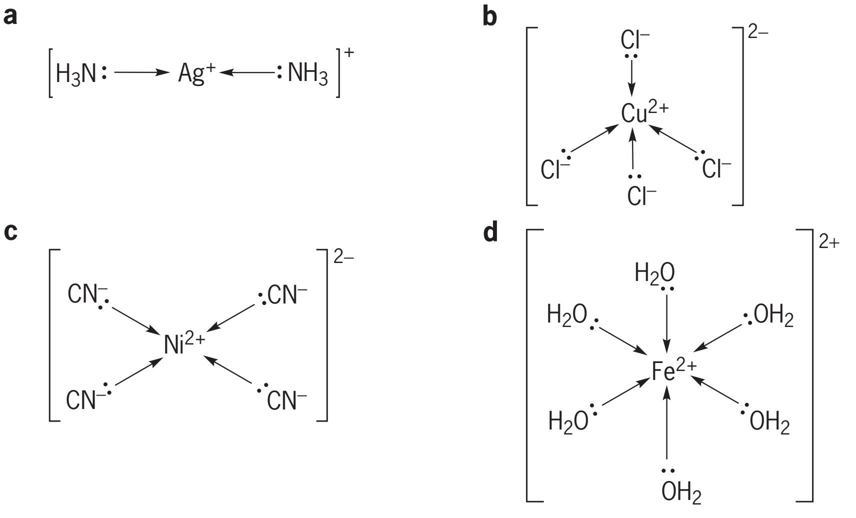


Figure 3.3.3 The four main shapes of complexes. (a) Linear, e.g. $[Ag(NH_3)_2]^+$, (b) tetrahedral, e.g. $[CuCl_4]^{2-}$, (c) square planar, e.g. $[Ni(CN)_4]^{2-}$, and (d) octahedral, e.g. $[Fe(H_2O)_6]^{2+}$.

Interactive Animation
Complex terminology

Complexes form most easily in solution. With a high enough concentration of the particular ligand, the transition metal ion will be surrounded by the ligands, which donate a non-bonding pair of electrons to the cation and form a coordinate or dative covalent bond. This means that the transition metal ion is behaving as a Lewis acid, an electron pair acceptor, and the ligand is a Lewis base, an electron pair donor (*Chemistry: For use with the IB Diploma Programme Standard Level*, chapter 9). When the complex is crystallized, most ligands stay in place; although, if the ligands are water molecules, some may be lost in the crystallization process.

$$[Cu(H_2O)_6]^{2+}(aq) \rightarrow [Cu(H_2O)_5]^{2+}(s) + H_2O(l)$$

Interactive Animation
Coordination number

The most common coordination numbers are four and six, although some complexes have only two ligands. According to VSEPR theory, the coordinate bonds take on the geometric arrangement that gives the complex the lowest energy. The shape of a complex with two ligands is linear, with four ligands it may be tetrahedral or square planar, and with six ligands the complex is octahedral. Silver ions often only form complexes with two ligands. This can be explained by the larger size and single positive charge (therefore lower charge density) of the silver ion. The copper(II) ion, Cu^{2+}, most commonly forms octahedral complexes with six ligands, although when a larger ligand such as the chloride ion, Cl^-, is involved, the complex is tetrahedral and only four ligands bond to the Cu^{2+} ion. Ligands that transfer a substantial amount of negative charge to the metal, such as CN^-, also produced reduced coordination numbers. Although six ammonia ligands can coordinate to Ni^{2+}, only four cyanide ions, CN^-, can coordinate, forming $[Ni(CN)_4]^{2-}$ which is square planar.

The formula for a complex includes all ligands and the overall charge is shown outside square brackets. Notice that the charge on the ligands will effect the overall charge on the complex.

When drawing the structures of complexes of d-block elements, the charge on the complex ion may be shown outside square brackets, or the square brackets may be omitted and the charge of the d-block ion shown directly on the ion.

CHEM COMPLEMENT

Saved by a chelating ligand

The ligands discussed so far have been monodentate ligands—they join to the metal ion by one atom only. Some polyatomic ligands are able to bond to the metal ion by means of two atoms (bidentate ligands) and others may bond by more than two atoms (polydentate ligands). Polydentate ligands generally form more stable complexes than the monodentate ligands. This great stability has medical uses.

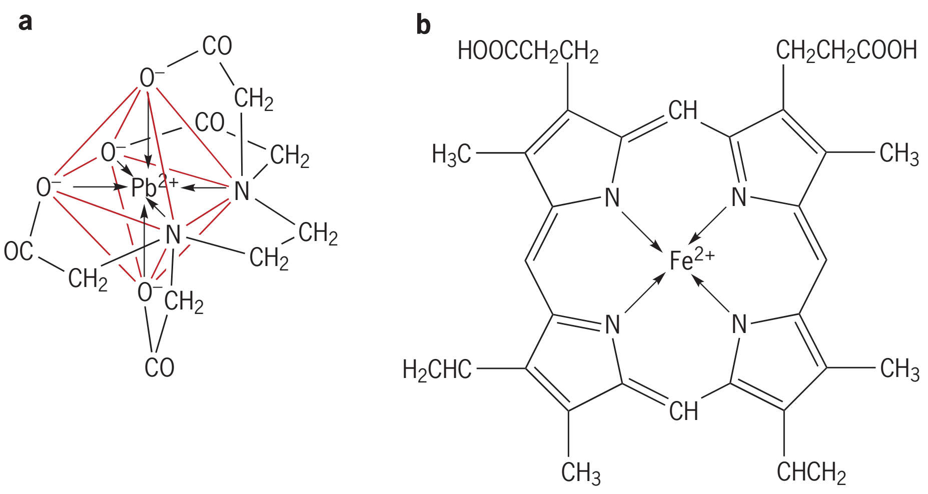


Figure 3.3.4 Two polydentate ligands. (a) EDTA complexed with a toxic lead(II) ion and (b) a porphyrin ring complexed with an iron(II) ion to make a heme group.

Ethylenediaminetetraacetate, EDTA, can be used to remove toxic aqueous ions such as lead and cadmium from the bodily fluids of patients suffering from poisoning. This process is called chelation. The EDTA ion has a 4− charge and can bond with the metal cation in six places. The formation of a complex between the EDTA and the toxic ion prevents the toxic ion from causing physiological damage. The porphyrin ring of the heme in hemoglobin is also a polydentate ligand.

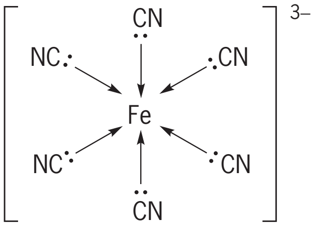
PRAC 3.1
Preparation of a transition metal complex

PRAC 3.2
Complexes of transition metals

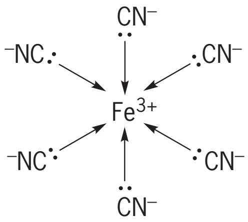
Worked example 1

Draw the structure of the hexacyanoferrate(III) ion $[Fe(CN)_6]^{3-}$.

Solution



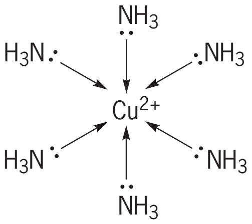
or



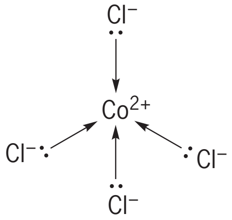
Worked example 2

State the formula of each of the following complexes.

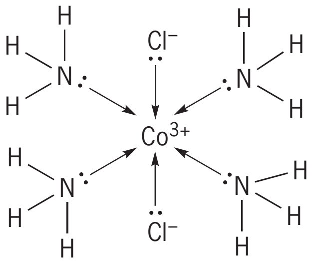
a



b



c



Solution

a The charge on the central ion is 2+, each NH_3 ligand is neutral, and so doesn't affect the overall charge of the complex. The formula of the complex is $[Cu(NH_3)_6]^{2+}$.

b The charge on the central ion is 2+, each Cl^- ligand has a 1– charge, and so four ligands have a charge of 4–. Overall charge is $+2 - 4 = -2$. The formula of the complex is $[CoCl_4]^{2-}$.

c The charge on the central ion is 3+, each Cl^- ligand has a 1– charge, and so two ligands have a charge of 2–. Each NH_3 is neutral, and so has no effect on the overall charge.

Overall charge is $+3 - 2 = +1$. The formula of the complex is $[CoCl_2(NH_3)_4]^+$.

Isomerism of transition metal complexes

Like organic compounds, a given transition metal complex can exist in a number of different structures. Two forms of isomerism that occur in transition metal complexes are ionization isomerism and stereoisomerism.

Worksheet 3.2
Transition metal complexes

Ionization isomerism

Ionization isomerism occurs in transition metal complex compound in which the elements are the same but the identity of the cation–anion pair varies. For example, $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are the same compound, but the sulfate and bromide ions have exchanged positions, thus changing the charge on the cation; that is, they are **ionization isomers**.

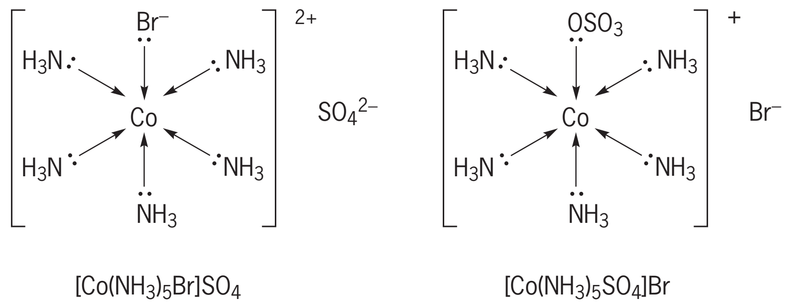


Figure 3.3.5 Ionization isomerism involves complex compounds in which the elements are the same but the identity of the cation–anion pair varies.

Stereoisomerism (geometric isomerism)

Geometric isomerism occurs in complexes with square planar or octahedral geometry. For a complex with two ligands of one type and two of another type in the square plane, there are two different arrangements possible of these ligands around the central ion. In the first **geometric isomer**, known as the *cis* isomer, the like ligands are in adjacent positions. In the second geometric isomer, the *trans* isomer, the like ligands are diagonally opposite each other. Biological systems are often sensitive to the difference between geometric isomers. A well-known example of this is the geometric isomer cisplatin, a chemotherapy drug. Its *trans* isomer, transplatin, does not work in the same way at all.

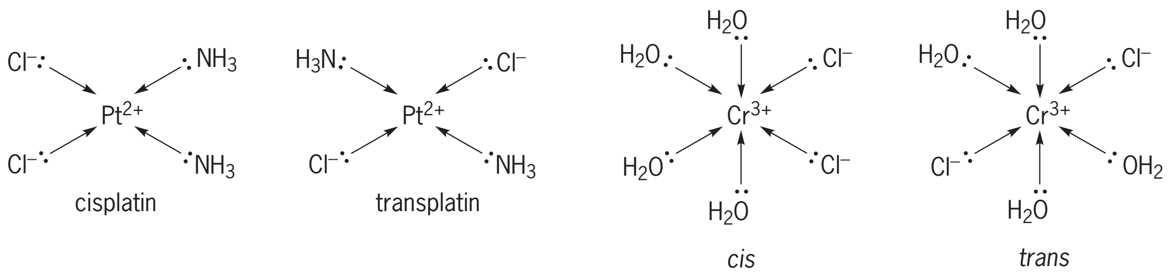


Figure 3.3.6 Geometric isomerism can be seen in square planar and octahedral complexes.

CHEM COMPLEMENT

Optical isomerism

In addition to exhibiting geometric isomerism, bidentate ligands such as 1,2-diaminoethane (ethylenediamine) and the ethanedioate (oxalate) ion can show another type of stereoisomerism, known as optical isomerism (see section 9.7). Optical isomers can be identified because their solutions can rotate plane-polarized light (see p. 327).

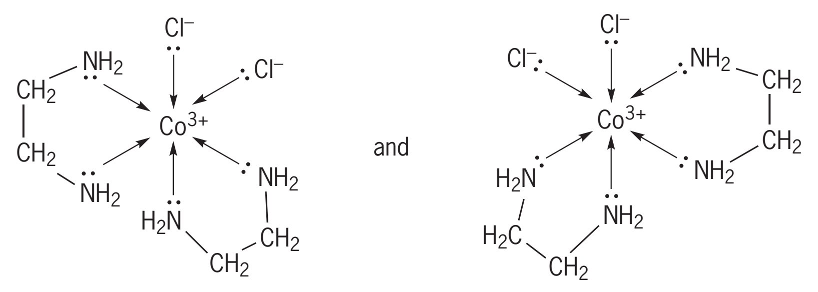


Figure 3.3.7 The two optical isomers of *cis*$[Co(en)_2Cl_2]^+$

The two different optical isomers rotate light in opposite directions. The complex is generally octahedral and has no plane of symmetry. The two structures are mirror images of each other. This phenomenon is also observed in organic compounds with a chiral centre (see section 9.7 p. 325). In figure 3.3.7 there are two optical isomers of the *cis*-diethylenediaminedichlorocobalt(III) ion, $[Co(NH_3)_4Cl_2]^+$.

Coloured d-block compounds

AS 13.2.6
Explain why some complexes of d-block elements are coloured.
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Compounds of groups 1, 2 and 3 are typically white. Similarly, compounds of zinc, one of the d-block elements which was not classified as a transition element, are also white. A characteristic property of the transition elements is that they form compounds that are brightly coloured.

Figure 3.3.8 Transition metal compounds exhibit a wide range of colours. From left to right the solutions are compounds of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu).

TABLE 3.3.2 SOME TRANSITION METAL COMPLEXES AND THEIR COLOURS

Formula	Colour
$[Fe(H_2O)_6]^{3+}$	Yellow
$[Fe(CN)_6]^{3-}$	Red
$[CuCl_4]^{2-}$	Yellow
$[Ag(NH_3)_2]^+$	Colourless
$[Co(H_2O)_6]^{2+}$	Pink
$[Cu(H_2O)_6]^{2+}$	Pale blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	Royal blue
cis-$[Co(NH_3)_4Cl_2]$	Violet
trans-$[Co(NH_3)_4Cl_2]$	Green

You will recall from your studies of the electromagnetic spectrum in the standard level course that white light is composed of a range of colours from red to violet. When white light hits an object, some is absorbed, some is reflected and (if the object is transparent) some is transmitted through it. The colour that we see when observing a substance is the result of some of the colours being removed from white light (by absorption and transmission). The colour that is observed is the complementary colour of the colour/s that has/have been absorbed. For example, if a solution appears to be a blue-green colour, it is absorbing orange-red light.

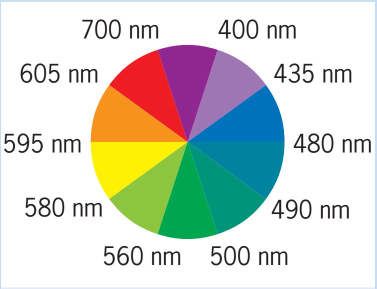


Figure 3.3.9 Complementary colours are opposite one another on a colour wheel. The colour of a substance that is observed is the complementary colour of the colour that has been absorbed.

The d orbitals of a transition metal ion that has formed coordinate bonds with ligands in a complex will be affected by the ligands surrounding the ion. Repulsion occurs between the non-bonding electrons of the ligand and the electrons in the d orbitals of the metal ion. Instead of being the same energy, as they are when the ion is isolated, the orbitals are split into two groups.

The closer a ligand can get to the metal ion the further apart the d orbitals will split. The amount of splitting depends on two factors:

1. the charge on the transition metal ion. An ion with a greater charge will attract the non-bonding pair of electrons on the ligand more strongly than one with a smaller charge, so the ligand will be pulled closer to this ion. This increases the repulsion between the non-bonding electrons of the ligand and the d-orbital electrons, increasing the splitting.
2. the size of the ligand. Smaller ligands can get closer to the metal ion, increasing the repulsion between the non-bonding electrons of the ligand and d-orbital electrons and increasing the splitting. The order of increasing amount of splitting for some common ligands is:

   $Cl^- < H_2O < NH_3 < CN^-$

For example, the chromium (III) ion, Cr^{3+}, has five 3d orbitals of the same energy. However, when the ion is surrounded by six water ligands, the five d orbitals are split into three orbitals of lower energy and two orbitals of higher energy.

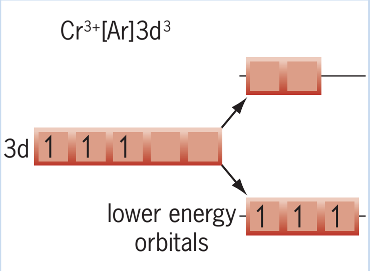


Figure 3.3.10 When the Cr^{3+} ion is surrounded by six water ligands, the five d orbitals are split into three orbitals of lower energy and two of higher energy.

When white light falls on the complex, energy is absorbed and electrons in the lower energy d orbitals are excited to a higher energy d orbital. The wavelength of energy absorbed depends on the difference in the energy of the split orbitals. The remaining wavelengths of the light combine to give the colour that is observed (the complementary colour).

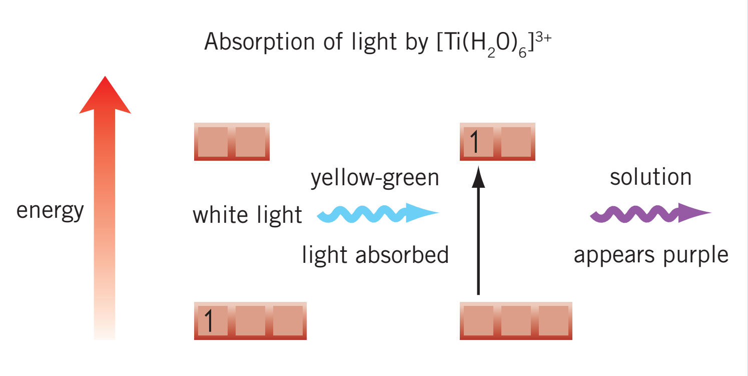


Figure 3.3.11 When white light is shone on $[Ti(H_2O)_6]^{3+}$ light in the yellow-green region is absorbed strongly, causing the solution to appear purple.

For example, if a complex ion absorbs light of a wavelength of 450 nm in the blue range of the visible light spectrum, then the ion appears yellow, its complementary colour in the opposite segment of the colour wheel. Similarly, for the hexaaquacopper(II) ion to appear blue it must absorb light with a wavelength of 580–595 nm.

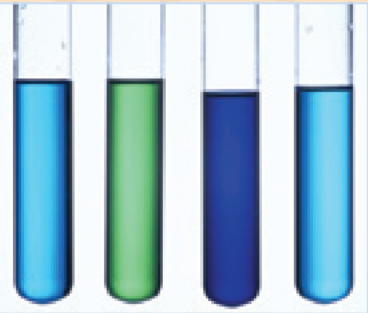


Figure 3.3.12 The colour of the copper ion solution depends on the ligands surrounding the copper ion. These four test tubes contain $[Cu(H_2O)_6]^{2+}$, $[CuCl_4]^{2-}$, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[Cu(EDTA)]^{2-}$.

Not all transition metal ions are coloured. If an ion does not have any d-orbital electrons, or the d orbital is full, there will be no electron transitions and compounds of the ion will appear colourless. For example:

- Cu^+—$[Ar]3d^{10}$—is colourless because it has a full 3d orbital.
- Ti^{4+}—$[Ar]$—is colourless because it has no 3d electrons.

The d-block ion $Sc^{3+}[Ar]$ is colourless because it has no 3d electrons and $Zn^{2+}[Ar]3d^{10}$ is colourless because it has a full 3d orbital. The absence of electrons in the 3d subshell or its complete filling do not prevent complexes being formed. The colourless tetrahydroxozinc(II) complex ion, $[Zn(OH)_4]^{2-}$, is formed when a solution containing hydroxide ions is added to a solution of Zn^{2+} ions.

Because the energies of the d orbitals are caused by the presence of ligands, it follows that different ligands will produce compounds of different colours. One of the most well-known examples of this is copper tetrammine, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, which is royal blue in colour, whereas the hexaaquo complex $[Cu(H_2O)_6]^{2+}$ is sky blue in colour. The reaction in which the water ligands are displaced by ammonia ligands is:

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

hexaaquacopper(II) ion	tetraamminediaquacopper(II) ion
sky blue	royal blue

The presence of ammonia ligands changes the energy of the d orbitals sufficiently to produce the more 'purplish' royal blue colour. (See Practical investigation 3.1.)

Another common example of the replacing of ligands to form a different complex involves the addition of 1.0 mol dm^{-3} ammonia to the $[Ni(H_2O)_6]^{2+}$ complex. The ammonia ligands replace all six water ligands:

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3\ (aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

hexaaquanickel(II) ion	hexaamminenickel(II)
green	blue

Section 3.3 Exercises

1 Compare a coordinate bond in a transition metal complex with a covalent bond found in a molecule such as ammonia.

2 Draw the structural formula of each of the following ligands, showing clearly their non-bonding pair of electrons.

a H_2O

b OH^-

c CN^-

d NH_3

3 Deduce the charge on each transition metal ion from the formula of its complex.

a $[Co(NH_3)_6]^{3+}$

b $[Co(NH_3)_5Cl]^{2+}$

c $[Cr(H_2O)_4Cl_2]^+$

4 Draw each of the following complex ions.

- **a** $[Co(NH_3)_6]^{3+}$
- **b** $[NiCl_4]^{2-}$
- **c** $[Ag(CN)_2]^-$

5 A solution of VO_2^+ is a bright yellow colour.

- **a** Deduce the colour of the light that is being absorbed by the solution.
- **b** State the oxidation state (oxidation number) of vanadium in the VO_2^+ ion.
- **c** Treatment of the VO_2^+ solution with zinc causes the colour to change to green, then to blue, then to green again and finally to violet. Without naming any of the compounds, explain what is happening to cause these colour changes.

6 Consider the following complex ions and predict the shape of each complex.

- **a** $[Fe(H_2O)_6]^{3+}$
- **b** $[Co(NH_3)_5Cl]^{2+}$
- **c** $[CuCl_4]^{2-}$
- **d** $[Ag(NH_3)_2]^+$
- **e** $[Ni(CN)_4]^{2-}$

7 Compare the electronic structures of complexes of Zn^{2+} and those of Cu^{2+} and hence explain why Zn^{2+} solutions are colourless whereas the Cu^{2+} complexes are coloured.

8 A complex ion can be formed between Fe^{3+} and the ligand CN^-.

- **a** Draw the structure of this complex ion.
- **b** Describe its shape.
- **c** Explain why the formula for this complex has a 3– charge.

9 A solution of copper(II) sulfate has some aqueous ammonia solution added and the colour changes from pale blue to a deep royal blue. Explain why this colour change has occurred.

10 Explain why $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be described as isomers.

Chapter 3 Summary

Terms and definitions

Alloy A mixture of a metal with one or more other elements.

Complex ion An ion formed when a small, highly charged transition metal ion forms coordinate bonds with a number of ligands.

Coordinate (dative) bond A covalent bond formed between two atoms, only one of which has provided electrons for the bond.

Coordination number The number of ligands surrounding a central metal ion in a complex.

d-block element An element whose highest energy electrons are filling a d subshell.

Geometric isomers Isomers that have different arrangements of their ligands around the central ion. They are named *cis* and *trans* according to the positioning of the ligands.

Heterogeneous catalyst A catalyst that is in a different state from the reactants it is catalysing.

Homogeneous catalyst A catalyst that is in the same state as the reactants it is catalysing.

Hydrated Surrounded by water molecules.

Ionization isomers Isomers of a transition metal complex in which the elements are the same but the identity of the cation–anion pair varies, e.g. $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.

Ligand A molecule or ion that has an electron pair that can be donated to the central metal ion.

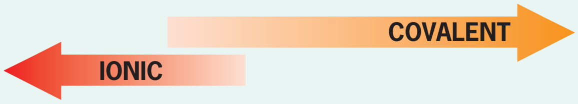
Standard conditions Temperature of 298 K, solution concentrations of 1 mol dm^{-3} and pressure of 1.01×10^2 kPa.

Transition element A d-block element that can form at least one stable ion with a partially filled d subshell.

Concepts

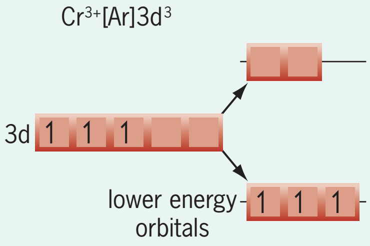
- Period 3 oxides and chlorides found on the left-hand side of the periodic table are solids, those in the middle are liquids and some on the right-hand side are gases.
- The period 3 oxides and chlorides that are solids under standard conditions conduct electricity when molten; however, the other period 3 oxides and chlorides do not conduct electricity.
- The period 3 oxides and chlorides exhibit ionic bonding with metals. The presence of ions that are free to move in the liquid state accounts for their ability to conduct electricity when molten.
- There is a gradual trend towards covalency in the bonding of the oxides and chlorides from left to right across period 3. Molecular compounds cannot conduct electricity due to an absence of free-moving charged particles.

Period 3	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
	$NaCl$	$MgCl_2$	Al_2Cl_3	$SiCl_4$	PCl_5	SCl_2	Cl_2



- Ionic chlorides such as NaCl and $MgCl_2$ dissolve in water and are surrounded by polar water molecules.
- Covalent chlorides such as $SiCl_4$ and PCl_5 react with water, forming acidic solutions.
- Transition metals:
  - exhibit a range of oxidation states
  - form coloured compounds
  - can form complexes
  - show catalytic properties as elements and compounds
  - have higher melting points and are harder and denser than main group (group 1 and group 2) metals.
- Transition elements are defined as elements that form at least one stable ion with a partially filled d subshell.
- Because scandium and zinc do not form any ions with a partially filled d subshell, they cannot be considered as transition elements.
- In forming ions, transition elements lose electrons initially from the 4s subshell and then from the 3d subshell. The similarity in energies of these two subshells makes it possible for an element to form a number of stable ions with different oxidation states.

- A ligand is an ion or a molecule with a non-bonding pair of electrons.
- A complex is formed when a small, highly charged transition metal ion forms coordinate bonds with a number of ligands. The number of ligands in a complex is most commonly 2, 4 or 6.
- The presence of ligands around a transition metal ion causes separation of the d orbitals to different energies. When light shines on the transition metal ion, some energy is absorbed by the electrons in the d orbitals and they are excited to a higher orbital. The light reflected or transmitted by the compound or solution is coloured due to the absence of some wavelengths of light from the original white light.



- Common catalysts involving transition elements are listed in this table.

Catalyst	**Reaction catalysed**
Platinum–rhodium alloy	Decomposition of NO in catalytic converter of car exhausts
Alloy of nickel and aluminium	Hydrogenation of alkanes
Manganese(IV) oxide, MnO_2	Decomposition of H_2O_2
Porous iron (can use osmium) (Haber process)	Production of ammonia
Vanadium(V) oxide pellets (Contact process)	Production of sulfuric acid

- In the human body transition metal ions are important as part of complexes that may act as catalysts for biochemical reactions. Examples of this include Co^{2+} in vitamin B_{12} and Fe^{2+} in the heme group of hemoglobin.

Chapter 3 Review questions

1 Classify each of the following period 3 oxides and chlorides according to their state and the type of bonding present under standard conditions:

magnesium chloride, $MgCl_2$
silicon dioxide, SiO_2
sodium oxide, Na_2O
aluminium oxide, Al_2O_3
chlorine, Cl_2
sulfur dioxide, SO_2

2 Explain why sulfur trioxide, SO_3, is a liquid under standard conditions whereas magnesium oxide, MgO, is solid.

3 Describe the reaction of phosphorus(V) chloride, PCl_5, with water and compare it with that of sodium chloride, NaCl, with water.

4 **a** Describe the structure of aluminium chloride when it is in the following state:

i solid
ii liquid
iii gaseous

b Use your answers to part **a** to explain why aluminium chloride does not conduct electricity in the:

i solid state
ii liquid state.

5 Consider the structure and bonding in the compounds NaCl and $SiCl_4$.

a Compare the electrical conductivity in the liquid state of these two compounds.

b Predict an approximate pH value for the solution formed when NaCl and $SiCl_4$ are added separately to different beakers of water.

6 State the full electron configuration of the following atoms and ions.

a Fe
b Cu^{2+}
c V^{3+}
d Mn

7 **a** Write the half-equation for the oxidation of Cr^{3+} to $Cr_2O_7{}^{2-}$.

b Describe the colour change that would accompany this reaction.

8 Describe three characteristic properties of a transition element.

9 Explain carefully why scandium and zinc are d-block metals but not transition metals.

10 Explain why an aqueous solution of $AlCl_3$ is considered to be acidic.

11 Discuss, listing at least two examples, the use of transition metals and their compounds as catalysts.

12 **a** Define the term *ligand*.

b Identify the ligands in the following list:

H_2O, OH^-, H^+, NH_3, NH_4^+, CN^-, Cl^-, CH_4

13 When $Cu^{2+}(aq)$ reacts with water to form the complex ion $[Cu(H_2O)_6]^{2+}$, a Lewis acid–base reaction occurs. Explain how the formation of $[Cu(H_2O)_6]^{2+}$ could be an acid–base reaction.

14 **a** Draw the complex ion formed between Ag^+ and NH_3.

b Annotate your drawing to describe the bonding in this complex ion.

15 Draw the complex ions formed between:

a Fe^{2+} and H_2O

b Cu^{2+} and Cl^-

c Ni^{2+} and CN^-

16 Outline the reasoning for the following statement, in terms of electronic configuration.

$Cr^{2+}(aq)$ is coloured and can behave as a reducing agent, whereas $Zn^{2+}(aq)$ is not coloured and does not behave as a reducing agent.

17 Consider the transition metal complex $K_3[Fe(CN)_6]$.

a Deduce the oxidation state of the iron in this complex.

b Identify the ligand in this complex and draw its structure.

c Write the full electron configuration of the iron in this complex.

d Use an orbital diagram (electrons in boxes) to show how many unpaired electrons are in the valence shell of iron when it is in this state.

18 **a** Explain why many d-block (transition metal) complexes are coloured.

b Name two examples of coloured transition metal complexes and one example of a non-coloured d-block metal complex.

19 For each of these transition elements:

i copper

ii vanadium

iii manganese

a State two possible oxidation states.

b Write the electron configuration for the transition element in the two oxidation states you have suggested in part **a**.

c State the formula of a compound in which the transition element is in that oxidation state.

20 Compare the elements of groups 1 and 2 to the first row transition elements, taking into consideration the:

a colour of compounds

b oxidation states

c physical properties of the elements

d types of compounds formed.

Web Destinations CW www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 3 Test

Part A: Multiple-choice questions

1 The compound $[Co(NH_3)_5Br]SO_4$ is isomeric with the compound $[Co(NH_3)_5SO_4]Br$. What is the oxidation state of cobalt in these compounds?

	$[Co(NH_3)_5Br]SO_4$	$[Co(NH_3)_5SO_4]Br$
A	+3	+3
B	+2	+1
C	+3	+2
D	+2	+3

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2 Which properties are typical of d-block elements?

I complex ion formation
II catalytic behaviour
III colourless compounds

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

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3 Which particles can act as ligands in complex ion formation?

I Cl^-
II NH_3
III H_2O

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

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4 Based on melting points, the dividing line between ionic and covalent chlorides of the elements Mg to S lies between:

A Mg and Al.
B Al and Si.
C Si and P.
D P and S.

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5 The colours of the compounds of d-block elements are due to electron transitions:

A between different d orbitals.
B between d orbitals and s orbitals.
C among the attached ligands.
D from the metal to the attached ligands.

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6 Which aqueous complex ion will **not** be coloured?

A Ni^{2+}
B Fe^{2+}
C Sc^{3+}
D Cr^{3+}

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7 Which electrons are lost by an atom of iron when it forms the Fe^{3+} ion?

A One s orbital electron and two d orbital electrons
B Two s orbital electrons and one d orbital electron
C Three s orbital electrons
D Three d orbital electrons

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8 Which oxidation number is the most common among the first row transition elements?

A +1
B +2
C +3
D +4

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9 Which is an essential feature of a ligand?

A A negative charge
B An odd number of electrons
C The presence of two or more atoms
D The presence of a non-bonding pair of electrons

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10 Which of the following oxides is (are) gas(es) at room temperature?

I SiO_2
II P_4O_6
III SO_2

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

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 This question is about period 3 elements and their compounds.

a Explain, in terms of structure and bonding, why silicon dioxide, SiO_2, has a high melting point.

(2 marks)

b Silicon tetrachloride, $SiCl_4$, reacts with water to form an acidic solution.

i Explain why silicon tetrachloride has a low melting point.

(2 marks)

ii Write an equation for the reaction of silicon tetrachloride with water.

(1 mark)

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2 Complex ions are a feature of the chemistry of d-block elements. For each of the following reactions give the formula of the complex ion formed and deduce its shape.

a Some iron metal is dissolved in sulfuric acid and left exposed to air until a yellow solution is formed.

(2 marks)

b A solution containing copper (II) ions is added to concentrated hydrochloric acid, forming a yellow solution.

(2 marks)

c A small amount of sodium hydroxide solution is added to silver nitrate solution. Ammonia solution is added until a colourless solution is obtained.

(2 marks)

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3 The elements in the d-block in the periodic table have several characteristics in common.

a Give the electronic configuration of Ni^{2+}.

(1 mark)

b Explain what is meant by a *ligand*, and describe the type of bond formed between a ligand and a d-block element.

(2 marks)

c Determine the oxidation numbers of copper in the species

$[Cu(NH_3)_4]^{2+}$ and $[CuCl_4]^{2-}$

(2 marks)

d Explain why the species in part **c** are coloured.

(3 marks)

e Identify the d-block element used as a catalyst in the Haber process and write an equation for the reaction occurring.

(2 marks)

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Part C: Data-based question

a Use the data in the table below to identify the type of bonding in each of the chlorides listed and state how the given properties depend on the type of bonding. Support your answer with appropriate diagrams.

Chloride	m.p. / K	b.p. / K
Sodium chloride	1074	1686
Aluminium chloride	451 sublimes	
Phosphorus(III) chloride	161	349

(9 marks)

b Describe how the chlorides behave when added to water. Give equations for any reactions which occur.

(5 marks)

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Part D: Extended-response question

Magnesium chloride and silicon(IV) chloride have very different properties.

a Give the formula and physical state at room temperature of each chloride.

(1 mark)

b State the conditions under which, if at all, each chloride conducts electricity.

(2 marks)

c Each chloride is added to water in separate experiments. Suggest an approximate pH value for the solution formed, and write an equation for any reaction that occurs.

(2 marks)

IBO HL Paper 2 Nov 06 Q6a

Total marks: 50

4

ENERGETICS

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 15: Energetics.

By the end of this chapter, you should be able to:

- define the terms *standard state*, *standard enthalpy change of formation* and *standard enthalpy change of combustion*
- calculate the standard enthalpy change of formation and the standard enthalpy change of combustion of a number of compounds
- use standard enthalpy changes of formation and combustion to determine the enthalpy change of a reaction
- define the term *lattice enthalpy*
- relate the lattice enthalpy of an ionic compound to the relative sizes and charges of the ions in it
- construct a Born–Haber cycle for group 1 and 2 chlorides and oxides, and use it to calculate one of the enthalpy changes in the cycle
- discuss how the difference between experimental and theoretical lattice enthalpies indicates the degree of covalent character in a compound
- determine whether an increase or decrease in entropy will occur in a chemical reaction by observation of the equation
- predict the sign and calculate the standard entropy change, $\Delta S^{\ominus}$, for a reaction
- use the sign of $\Delta G^{\ominus}$ to determine whether or not a reaction will be spontaneous
- use the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ to calculate a value for $\Delta G^{\ominus}$ for a reaction
- calculate $\Delta G^{\ominus}$ using free energy change of formation, $\Delta G_f^{\ominus}$ data
- predict the effect of a change in temperature on the spontaneity of a reaction.

IBO Assessment statements 15.1.1. to 15.4.3

In our study of energetics to this point we have mainly been concerned with thermochemistry—the study of energy transfers between reacting chemicals and their surroundings. We have found that the enthalpy of a reaction can be determined by experimental and some theoretical means. Energetics also encompasses the study of thermodynamics—the scientific study of the relationships between heat, work and energy. Work is done on an object when you transfer energy to that object.

The laws of thermodynamics are fundamental laws of physics that bind together our studies of chemistry.

First law: Energy can neither be created nor destroyed; it is conserved. This law is fundamental to the balancing of chemical equations.

Second law: The entropy of an isolated system (when not in equilibrium) will tend to increase over time. We will investigate this law in our studies of entropy in section 4.3.

Third law: As a system approaches absolute zero (0 K) of temperature, all processes cease and the entropy of the system approaches a minimum value (zero). The effect of temperature and entropy on the free energy of a reaction (its spontaneity) will be investigated in section 4.4.

4.1 STANDARD ENTHALPY CHANGES OF REACTION

AS 15.1.1
Define and apply the terms *standard state, standard enthalpy change of formation* ($\Delta H_f^\ominus$) and *standard enthalpy change of combustion* ($\Delta H_c^\ominus$).
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A chemical reaction occurring in the laboratory does not exist in isolation. It has surroundings to which it may release heat (an exothermic reaction) or from which it can absorb heat (an endothermic reaction). The reaction being studied can be referred to as 'the system' and it is separated from the surroundings by a boundary. Together the system and its surroundings can be referred to as the 'universe'. If heat is unable to escape or enter the system, this must be because the system is thermally insulated. In the case of a closed system, matter is unable to enter or leave the system.

The heat flow into or out of a system at constant pressure is known as **enthalpy** and is represented by the symbol H. Since the absolute enthalpy of a substance cannot be determined, we measure the change in enthalpy, ΔH.

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

When the enthalpy change is measured under standard conditions at 298 K and 101.3 kPa pressure, it is referred to as a standard enthalpy change. This is written as $\Delta H^\ominus$. Enthalpy changes can be identified specifically by the type of reaction for which they are measured. The enthalpy change for a combustion reaction such as

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

measured under standard conditions is known as the **standard enthalpy change of combustion**, $\Delta H_c^\ominus$. Notice that all reactants and products are in their **standard state**—the state in which they would be found at 298 K and a pressure of 1.01×10^2 kPa.

CHEM COMPLEMENT

Marsh lights

When organic matter such as plant material is decomposed by bacteria under water, where oxygen is not in abundance (anaerobic conditions), methane, CH_4, is produced. Methane produced in this manner was known historically in England as marsh gas. It is believed that spontaneous combustion of this marsh gas produced an eerie pale blue light in marshes and bogs. Such a light was known as a marsh light. Legends in England were told of unwary travellers who were lured off safe paths by these marsh lights and drowned in the marsh. Similar conditions exist in rice paddies and wetlands, so it is likely that these eerie lights are also seen in these areas.

Figure 4.1.1 Pale blue marsh lights appeared in the middle of dark bogs or marshes due to the spontaneous combustion of methane.

The standard enthalpy change of combustion of a fuel such as methane could be measured using a bomb calorimeter in which the amount of heat energy released by the reaction is determined by finding the change in temperature of a body of water surrounding the reaction vessel.

Although there is no way in which the absolute enthalpy of a substance can be determined experimentally, the enthalpy of a substance can be measured relative to an arbitrary reference. The arbitrary reference point to which enthalpies are compared is called the **standard enthalpy change of formation**, $\Delta H_f^\ominus$. The standard enthalpy change of formation is defined as the enthalpy change that results when one mole of a compound is formed from its elements at a pressure of 1.01×10^2 kPa and 298 K.

By convention, the standard enthalpy change of formation of any element in its most stable form is zero.

For example, there are two allotropic forms of the element oxygen—oxygen gas, O_2, and ozone, O_3. Oxygen gas is the more stable form of oxygen, so $\Delta H_f^\ominus(O_2) = 0$ kJ mol^{-1}, but $\Delta H_f^\ominus(O_3) = +142.2$ kJ mol^{-1}.

Figure 4.1.2 The standard enthalpy change of combustion could be measured in a bomb calorimeter.

TABLE 4.1.1 STANDARD ENTHALPIES OF FORMATION OF SELECTED COMPOUNDS

(Some of these values can also be found in Appendix 3 and in table 11 of the IB Data booklet. © IBO 2007)

Substance	Formula	State	$\Delta H_f^\ominus$ (kJ mol^{-1})	Substance	Formula	State	$\Delta H_f^\ominus$ (kJ mol^{-1})
Ammonia	NH_3	g	–46	Ethyne	C_2H_2	g	+227
Ammonium bromide	NH_4Br	s	–271	Hydrogen bromide	HBr	g	–36
Butane	C_4H_{10}	g	–125	Methane	CH_4	g	–75
But-1-ene	C_4H_8	g	+1	Nitrogen monoxide	NO	g	+90
Carbon dioxide	CO_2	g	–394	Pentane	C_5H_{12}	l	–173
Ethane	C_2H_6	g	–85	Propane	C_3H_8	g	–104
Ethanol	C_2H_5OH	g	–235	Propene	C_3H_6	g	+20
Ethene	C_2H_4	g	+52	Water	H_2O	g	–242
Ethylamine	$C_2H_5NH_2$	g	–49	Water	H_2O	l	–286

Worked example 1

Write the chemical equation, including state symbols, representing the standard enthalpy of formation of nitric acid.

Solution

The standard enthalpy of formation of a compound is the enthalpy change that results when one mole of a compound is formed from its elements at a pressure of 1.01×10^2 kPa and 298 K, so this equation should have the reactants H_2, N_2 and O_2 and the product HNO_3. All states should be those that occur under standard conditions. Note that this is a theoretical equation only.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}N_2(g) + 1\tfrac{1}{2}O_2(g) \rightarrow HNO_3(l)$$

AS 15.1.2 Determine the enthalpy change of a reaction using standard enthalpy changes of formation and combustion. ©IBO 2007

Standard enthalpy changes of formation can be used to calculate the **standard enthalpy change of reaction**, $\Delta H^{\ominus}_{rxn}$. This is defined as the enthalpy change of a reaction when carried out at 298 K and at a pressure of 1.01×10^2 kPa.

Let us consider a hypothetical reaction

$$aA + bB \rightarrow cC + dD$$

in which *a* mol of A reacts with *b* mol of B to make *c* mol of C and *d* mol of D.

The standard enthalpy of reaction, $\Delta H^{\ominus}_{rxn}$ can be calculated using the $\Delta H^{\ominus}_{f}$ values for the reactants and products in a similar way to which we defined the enthalpy change for a reaction:

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

$$\Delta H^{\ominus}_{rxn} = [c\Delta H^{\ominus}_{f}(C) + d\Delta H^{\ominus}_{f}(D)] - [a\Delta H^{\ominus}_{f}(A) + b\Delta H^{\ominus}_{f}(B)]$$

$$= \Sigma n\Delta H^{\ominus}_{f}(\text{products}) - \Sigma m\Delta H^{\ominus}_{f}(\text{reactants})$$

where Σ (sigma) means 'the sum of' and *m* and *n* represent the stoichiometric coefficients for the reactants and products.

Although standard enthalpies of formation are often tabulated and readily available, it may sometimes be necessary to determine the standard enthalpy of formation of a compound before it can be used elsewhere. This may be done using the equation for the formation of that compound from its elements and other data such as enthalpy of combustion.

For example, carbon dioxide is formed when graphite burns in oxygen according to the equation:

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\ominus}_{c} = -394 \text{ kJ mol}^{-1}$$

This equation illustrates the standard enthalpy of formation of carbon dioxide and is also the equation for the combustion of graphite.

We can use this equation and the standard enthalpy change of combustion of graphite, $\Delta H^{\ominus}_{c}(C(\text{graphite}))$, to find the standard enthalpy of formation of carbon dioxide. Both oxygen and graphite are the most stable allotropic forms of the elements (oxygen and carbon), so their standard enthalpies of formation are both equal to zero.

The standard enthalpy change of combustion, $\Delta H_c^\ominus$ for graphite has been given as –394 kJ mol^{-1} (such values are also tabulated), so we can calculate the standard enthalpy of formation of the product, carbon dioxide:

$$\Delta H_c^\ominus(\text{C(graphite)})$$
$$= [(1\ \text{mol})\Delta H_f^\ominus(CO_2)] - [(1\ \text{mol})\Delta H_c^\ominus(\text{graphite}) + (1\ \text{mol})\Delta H_f^\ominus(O_2)]$$

Rearranging the equation to make the unknown quantity, the standard enthalpy of formation of CO_2, the subject and substituting in the value for ΔH(C(graphite)) gives:

$$\Delta H_f^\ominus(CO_2) = -394\ \text{kJ mol}^{-1} + [(1\ \text{mol})\ \Delta H_f^\ominus(\text{graphite}) + (1\ \text{mol})\Delta H_f^\ominus(CO_2)]$$
$$\Delta H_f^\ominus(CO_2) = -394\ \text{kJ mol}^{-1} + [(0\ \text{kJ mol}^{-1}) + (0\ \text{kJ mol}^{-1})]$$
$$\Delta H_f^\ominus(CO_2) = -394\ \text{kJ mol}^{-1}$$

It is important to remember the basic structure of a combustion reaction. A fuel, such as methane, reacts with oxygen to form carbon dioxide and water. The equation above for graphite was a little simpler, since graphite is an element; however, this pattern is the same for all hydrocarbons, including alcohols.

Complete combustion: fuel + oxygen → carbon dioxide + water

Worked example 2

Use the information in table 4.1.1 to calculate the enthalpy change for the complete combustion of ethene according to the following equation:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Solution

$$\Delta H_c^\ominus = \sum n\Delta H_f^\ominus(\text{products}) - \sum m\Delta H_f^\ominus(\text{reactants})$$
$$\begin{aligned}\Delta H_c^\ominus &= [(2\ \text{mol})\Delta H_f^\ominus(CO_2) + (2\ \text{mol})\Delta H_f^\ominus(H_2O)] - [(1\ \text{mol})\Delta H_f^\ominus(C_2H_4)\\ &\quad + (3\ \text{mol})\ (O_2)]\\ &= [(2\times -394) + (2\times -242)] - [+52 + (3\times 0)]\\ &= -788 - 484 - 52\\ &= -1324\ \text{kJ mol}^{-1}\end{aligned}$$

Worked example 3

Find $\Delta H_{rxn}^\ominus$ for the acid–base reaction between ammonia and hydrogen bromide using standard enthalpy changes of formation in table 4.1.1.

Solution

$$NH_3(g) + HBr(g) \rightarrow NH_4Br(s)$$

Standard enthalpy changes of formation:

$$\begin{aligned}\Delta H_{rxn}^\ominus &= \sum n\Delta H_f^\ominus(\text{products}) - \sum m\Delta H_f^\ominus(\text{reactants})\\ &= -271 - (-46 + -36)\\ &= -271 - (-82)\\ &= -189\ \text{kJ mol}^{-1}\end{aligned}$$

You should recall a few important points about thermochemical equations from your standard level course.

- The coefficients in a thermochemical equation should always be taken as actual amounts, unlike other equations in which they are just giving an indication of the molar ratio in which the substances react.
- When a thermochemical equation is reversed, the sign of the enthalpy change is also reversed.
- When the coefficients in a thermochemical equation are multiplied by a factor *n*, the value of the enthalpy change is multiplied by that same factor.
- States are very important in thermochemical equations and change the value of the enthalpy change, so they must always be specified. For example, in the combustion of methane:

  $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c^\ominus = -890.4 \text{ kJ mol}^{-1}$$

  Yet when the same equation is written with water vapour as the product instead of liquid water:

  $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H_c^\ominus = -802.4 \text{ kJ mol}^{-1}$$

  This difference is caused by the endothermic reaction in which two mole of liquid water is evaporated:

  $$2H_2O(l) \rightarrow 2H_2O(g) \qquad \Delta H = +88 \text{ kJ mol}^{-1}$$

Worked example 4

Construct a simple enthalpy cycle and calculate the standard enthalpy change of formation for $CH_3OH(l)$ given the following data.

Compound	$\Delta H_f^\ominus$ (kJ mol^{-1})	$\Delta H_c^\ominus$ (kJ mol^{-1})
$H_2O(l)$	−286	
$CO_2(g)$	−394	
$CH_3OH(l)$		−715

Solution

Note that while $\Delta H_c^\ominus(CH_3OH) = -715$ kJ mol^{-1}, for the balanced equation below

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H = -1430 \text{ kJ mol}^{-1}$$

since 2 mol of $CH_3OH(l)$ are required to balance the equation.

$$\begin{aligned}\Delta H_{rxn}(CH_3OH) = \Delta H^\ominus_{rxn} &= \Sigma n\Delta H_f^\ominus(\text{products}) - \Sigma m\Delta H_f^\ominus(\text{reactants})\\ &= [(2\text{ mol})\Delta H_f^\ominus(CO_2) + (4\text{ mol})\Delta H_f^\ominus(H_2O)]\\ &\quad - [(2\text{ mol})\Delta H_f^\ominus(CH_3OH) + (3\text{ mol})\Delta H_f^\ominus(O_2)]\end{aligned}$$

Rearranging the equation to make $(2\text{ mol})\Delta H_f^\ominus(CH_3OH)$ the subject gives:

$$\begin{aligned}(2\text{ mol})\Delta H_f^\ominus(CH_3OH) = {}&[(2\text{ mol})\Delta H_f^\ominus(CO_2) + (4\text{ mol})\Delta H_f^\ominus(H_2O)]\\ &- [(3\text{ mol})\Delta H_f^\ominus(O_2)] - \Delta H_{rxn}(CH_3OH)\end{aligned}$$

Substitute the values given for $\Delta H_f^\ominus$ and $\Delta H_c^\ominus$ into this equation:

$$\begin{aligned}2 \times \Delta H_f^\ominus(CH_3OH) &= [(2 \times -394) + (4 \times -286)] - [(3\text{ mol}) \times 0] - (1430)\\ &= -502\\ \Delta H_f^\ominus(CH_3OH(l)) &= -251 \text{ kJ mol}^{-1}\end{aligned}$$

Section 4.1 Exercises

1 The enthalpy change of the following reaction is negative:

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

Describe how the stabilities of the reactants compare with those of the products.

2 Define the term *standard enthalpy change of formation*, $\Delta H_f^\ominus$, and illustrate your answer with an equation, including state symbols, for the formation of methane, CH_4.

3 Explain why the standard enthalpy of formation of graphite is equal to zero, while that of diamond is +1.90 kJ mol^{-1}.

4 The standard enthalpy change of formation of $C_2H_5OH(g)$ is –235 kJ mol^{-1}. Predict how the value of $\Delta H_f^\ominus$ for $C_2H_5OH(l)$ would compare with this value and explain your answer.

5 The standard enthalpy change of formation values for two oxides of sulfur are:

$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H_f^\ominus = -296.1\ \text{kJ mol}^{-1}$

$S(s) + \frac{3}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H_f^\ominus = -395.2\ \text{kJ mol}^{-1}$

Calculate the enthalpy change, in kJ mol^{-1}, for the reaction:

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

6 Ethyne (also known as acetylene), C_2H_2, is commonly used as a fuel for the high-temperature flame used in welding. The equation for the combustion of ethyne is:

$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$

Calculate the standard enthalpy change of combustion for ethyne, using values from table 4.1.1.

7 Ethylamine can be manufactured by the reaction:

$C_2H_5OH(g) + NH_3(g) \rightarrow C_2H_5NH_2(g) + H_2O(g)$

Use values from table 4.1.1 to calculate the enthalpy change for this reaction.

8 Using values from table 4.1.1, calculate the standard enthalpy of combustion for propene, given the equation for the reaction:

$2C_3H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

9 Construct a simple enthalpy cycle and calculate the standard enthalpy change of formation of propanol, $C_3H_7OH(l)$, given the information in table 4.1.1 and that the standard heat of combustion of propanol is –2010 kJ mol^{-1}.

10 The standard enthalpy change of combustion of ethanal, $CH_3CHO(l)$, is –1167 kJ mol^{-1}. Given the information in table 4.1.1, calculate the standard enthalpy change of formation of ethanal.

4.2 LATTICE ENTHALPY AND BORN–HABER CYCLES

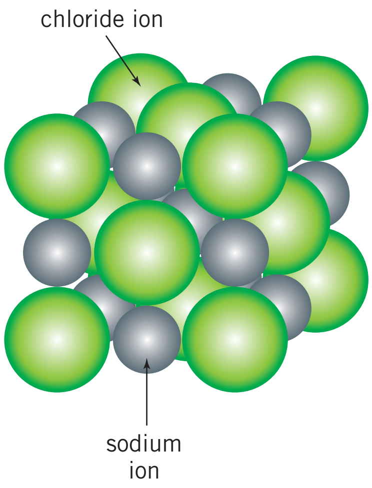


Figure 4.2.1 Ionic solids, such as sodium chloride, are made up of a lattice of positive and negative ions.

While our calculations to this point have generally involved the formation of molecular substances, there is an important group of compounds that need to be investigated—ionic compounds.

You will recall that an ionic compound exists as a crystal lattice in which positive and negative ions alternate and which is held together by the electrostatic attraction between these positive and negative ions.

How can we evaluate the stability of an ionic compound? We know that they have very high melting temperatures, but there certainly is a difference between ionic compounds. The stability of an ionic compound depends on the interaction between cations and the specific number of anions surrounding them and vice versa, not simply the interaction between a single cation and a single anion. The **lattice enthalpy** of an ionic solid provides a quantitative measure of its stability. It is defined as the energy required to completely separate one mole of a solid ionic compound into its gaseous ions. It cannot be measured directly, but instead can be be calculated indirectly by assuming that the formation of the ionic lattice occurs by a number of steps.

> **The lattice enthalpy of an ionic solid is the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.**

AS **15.2.1**
Define and apply the terms *lattice enthalpy* and *electron affinity*. © IBO 2007

By applying Hess's law to the standard enthalpy changes that occur when an ionic compound is formed, the lattice enthalpies of ionic compounds can be related to ionization energies, electron affinities and other atomic and molecular properties. This is called a Born–Haber cycle.

CHEM COMPLEMENT

Max Born and Fritz Haber

How does a theoretical process come to be named after two people? Fritz Haber, a German chemist, was the winner of the Nobel Prize for Chemistry in 1918 for his work in the synthesis of ammonia from nitrogen and hydrogen. A lot of Haber's work was done as a member of the German military during World War I. Before and after that war he was director of the Institute for Physical and Electrochemistry (the Kaiser Wilhelm Institute) at Berlin-Dahlem. Part of his interest in electrochemistry led him to the study of electrolysis of salts.

Max Born, also German, won the Nobel Prize in Physics in 1954 for his work in quantum theory. He also was part of the scientific branch of the German armed forces during World War I and published a book on crystal theory during that time. After the war he worked at the University of Göttingen and completed further work on crystal lattices.

Both scientists knew James Franck, a German physicist who worked at both universities during the years after World War I. Although Born and Haber never worked together in a university, the method for determining the lattice enthalpy of an ionic crystal is named after both of them. Did they collaborate during World War I, or did James Franck help them to combine their work?

The ionization energy of an element involves the removal of electrons from atoms to create positive ions. The definition of ionization energy emphasizes that the atoms and ions be in the gaseous state, since the energy involved in ionization must only be that required to remove the electron from the atom or ion, not a combination of energy that would change the state of the element and then remove an electron.

Similarly, **electron affinity** requires the element to be in the gaseous state.

> **Electron affinity is the energy change that occurs when one mole of electrons is accepted by one mole of atoms in the gaseous state to form one mole of negative ions.**

Other atomic and molecular processes that must occur in order for elemental metals and non-metals to form an ionic lattice include the vaporization of solids, the dissociation of molecules into individual atoms and the final reaction between gaseous ions to form a solid compound.

AS **15.2.3 Construct a Born–Haber cycle for group 1 and 2 oxides and chlorides, and use it to calculate an enthalpy change. © IBO 2007**

The enthalpy values that are involved in a Born–Haber cycle are as follows.

1. Atomization of the solid metal: $\Delta H^\ominus_{at}$
2. Ionization of the gaseous metal: $\Delta H^\ominus_{I}$
3. Dissociation or atomization of the molecular non-metal into atoms: $\Delta H^\ominus_{D}$.
4. Addition of electrons to the non-metal atoms (electron affinity): $\Delta H^\ominus_{E}$.
5. Reaction between the gaseous ions to form the solid ionic lattice: $\Delta H^\ominus_{lf}$.

The last step, the enthalpy of formation of the ionic compound $\Delta H^\ominus_{lf}$ has the same magnitude but the opposite sign to the lattice enthalpy of the compound, $\Delta H^\ominus_{L}$.

A Born–Haber cycle combines all of the above steps to determine one that cannot be measured. This may be the overall enthalpy for the reaction of the solid metal with a gaseous non-metal to form a solid ionic compound, or it may be one of the steps that is unobtainable, such as the electron affinity of the non-metal.

The processes of atomization and ionization are both endothermic. Energy must be added to remove an electron, to change state from solid to gas, or to separate the atoms in a molecule. The electron affinity is exothermic. Energy is released when an electron is added to a non-metal atom; as the atom is acquiring greater stability, its energy is decreasing. The formation of the solid ionic lattice from the gaseous ions must be a sufficiently exothermic reaction to make up for the energy used in the early steps. Unless the standard enthalpy change of formation is exothermic, the compound will not form, or at best will be thermally unstable.

> **As a general rule, the more negative the standard enthalpy change of formation of the ionic compound, the more stable the compound will be.**

Worked example 1

Find the overall enthalpy for the formation of solid sodium chloride from sodium and chlorine, according to the equation:

$$\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl(s)}$$

Solution

1 Atomization of sodium:

$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)}$ $\quad \Delta H^\ominus_{at} = +108\ \mathrm{kJ\ mol^{-1}}$

2 Ionization of sodium:

$\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{e^-}$ $\quad \Delta H^\ominus_{I} = +494\ \mathrm{kJ\ mol^{-1}}$

3 Dissociation (atomization) of chlorine molecules:

$Cl_2(g) \rightarrow 2Cl(g) \qquad \Delta H^{\ominus}_{D} = +244\ \text{kJ mol}^{-1}$

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \qquad \frac{1}{2}\Delta H^{\ominus}_{D} = +122\ \text{kJ mol}^{-1}$

4 Ionization (electron affinity) of chlorine atoms:

$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H^{\ominus}_{E} = -349\ \text{kJ mol}^{-1}$

5 Reaction between ions:

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^{\ominus}_{lf} = -787\ \text{kJ mol}^{-1}$

According to Hess's law we can write:

$$\begin{aligned}\Delta H^{\ominus}_{f} &= \Delta H^{\ominus}_{at} + \Delta H^{\ominus}_{I} + \tfrac{1}{2}\Delta H^{\ominus}_{D} + \Delta H^{\ominus}_{E} + \Delta H^{\ominus}_{lf}\\ &= 108 + 494 + 122 + (-349) + (-787)\\ &= -412\ \text{kJ mol}^{-1}\end{aligned}$$

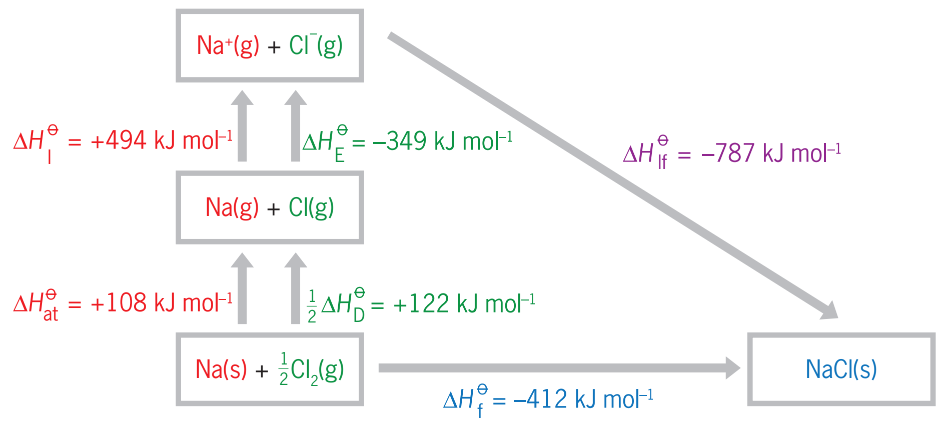


Figure 4.2.2 The Born–Haber cycle for the formation of solid NaCl.

Lattice enthalpy of NaCl:

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

has the same value as $\Delta H^{\ominus}_{lf}$, but opposite sign = +787 kJ mol^{-1}.

Worked example 2

Construct a Born–Haber cycle for the formation of magnesium oxide, MgO, labelling the cycle with the formulas and state symbols of the species present at each stage.

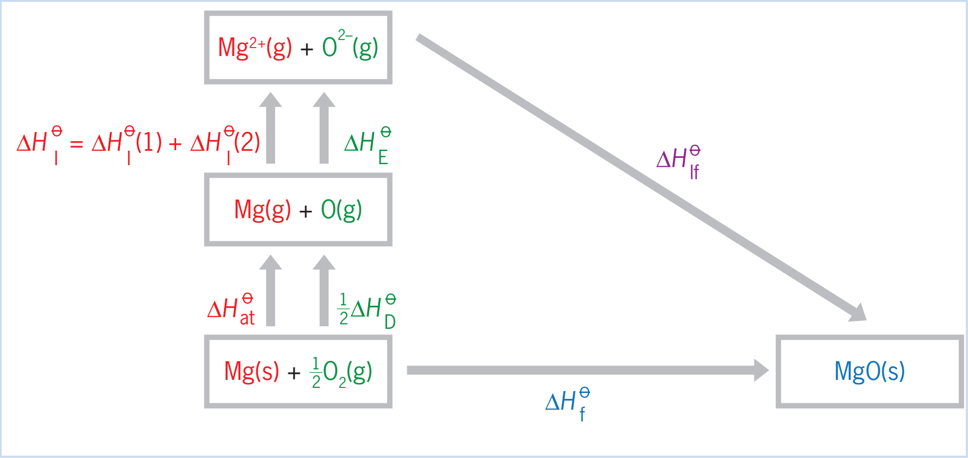
Solution

Note that since magnesium forms Mg^{2+}, the enthalpy of ionization is the sum of the first and second ionization enthalpies of magnesium.

$Mg(g) \rightarrow Mg^+(g) + e^- \quad \Delta H^{\ominus}_{I}(1)$

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \quad \Delta H^{\ominus}_{I}(2)$

$\Delta H^{\ominus}_{I} = \Delta H^{\ominus}_{I}(1) + \Delta H^{\ominus}_{I}(2)$



Worked example 3

Find the overall enthalpy for the reaction between magnesium and chlorine according to the equation:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

and construct a Born–Haber cycle for the formation of magnesium chloride, $MgCl_2$. Label the cycle with the formulas and state symbols of the species present at each stage.

WORKSHEET 4.1
Born–Haber cycles

Solution

1 Atomization of magnesium:

$Mg(s) \rightarrow Mg(g) \qquad \Delta H_{at}^\ominus = +148 \text{ kJ mol}^{-1}$

2 Ionization of magnesium:

$Mg(g) \rightarrow Mg^+(g) + e^- \qquad \Delta H_I^\ominus(1) = +736 \text{ kJ mol}^{-1}$
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \qquad \Delta H_I^\ominus(2) = +1451 \text{ kJ mol}^{-1}$
$\Delta H_I^\ominus = \Delta H_I^\ominus(1) + \Delta H_I^\ominus(2) = +2187 \text{ kJ mol}^{-1}$

3 Dissociation (atomization) of chlorine molecules:

(Note that 2 mol of chlorine atoms are required.)

$Cl_2(g) \rightarrow 2Cl(g) \qquad \Delta H_D^\ominus = +244 \text{ kJ mol}^{-1}$

4 Ionization (electron affinity) of chlorine atoms:

$2Cl(g) + 2e^- \rightarrow 2Cl^-(g) \qquad \Delta H_E^\ominus = 2 \times -349 = -698 \text{ kJ mol}^{-1}$

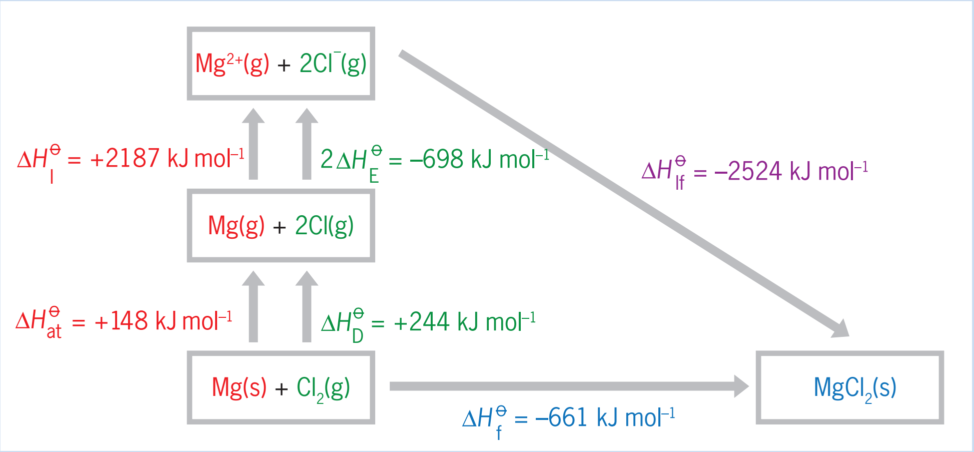
5 Reaction between ions:

$Mg^{2+}(g) + 2Cl^-(g) \rightarrow MgCl_2(s) \quad \Delta H_{lf}^\ominus = -2524 \text{ kJ mol}^{-1}$

According to Hess's law we can write:

$$\begin{aligned}\Delta H_f^\ominus &= \Delta H_{at}^\ominus + \Delta H_I^\ominus + \Delta H_D^\ominus + \Delta H_E^\ominus + \Delta H_{lf}^\ominus \\ &= 148 + 2187 + 244 + (-698) + (-2542) \\ &= -661 \text{ kJ mol}^{-1}\end{aligned}$$

Note that the molar ratio of the two ions in $MgCl_2$ is 1:2, so in comparison to that of NaCl, all quantities related to chlorine in this Born–Haber cycle are doubled.



Comparing the stability of different ionic compounds

15.2.2 Explain how the relative sizes and the charges of ions affect the lattice enthalpies of different ionic compounds. © IBO 2007

Our model of ionic bonding represents each ion as a sphere with its charge uniformly distributed over the surface.

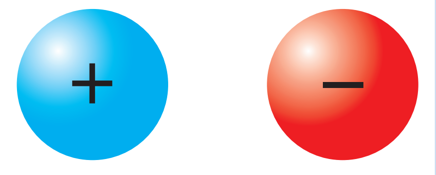


Figure 4.2.3 Ions are modelled as spheres with their charge uniformly distributed over the surface.

Theoretical values of lattice enthalpies can be calculated from knowledge of the charges on the ions and the distance between the ions.

$$\text{Lattice enthalpy} \propto \frac{(\text{charge on cation}) \times (\text{charge on anion})}{\text{sum of ionic radii}}$$

The greater the lattice enthalpy, the more stable the ionic compound will be and the more tightly the ions will be held together, so the higher the melting point will be. The following table compares the lattice enthalpies of some ionic compounds that have an ion in common.

TABLE 4.2.1 SOME LATTICE ENTHALPIES AND IONIC CHARGE AND SIZES

Lattice enthalpies (kJ mol^{-1})		Ionic radii (10^{-12} m)	
NaCl	+771	Na^+	98
KCl	+701	K^+	133
		Cl^-	181
NaF	+902	Na^+	98
NaBr	+733	F^-	133
NaI	+684	Br^-	196
		I^-	219
MgF_2	+2957	Mg^{2+}	65
NaF	+902	Na^+	98
		F^-	133

Why do both the charge and the size of the ions influence the lattice enthalpy of an ionic compound? The size of the force of attraction, F, of one ion on another is given by Coulomb's law:

$$F = k\frac{q_1 q_2}{r^2}$$

where q_1 and q_2 are the charges on the two ions and r is the distance between them (the sum of their radii).

We can see from this relationship that the force of attraction, F, will increase when the charge on one or other of the ions increases and when the distance between the two ions decreases. (The denominator of the fraction will decrease, so the force of attraction, F, will increase.) This can be seen clearly when we compare pairs of ionic compounds from table 4.2.1.

1 NaCl and KCl

In this pair of compounds, the cations are different, but the anion stays the same. Na^+ and K^+ have the same charge, but the ionic radius of K^+ is considerably greater than that of Na^+, due to the extra shell of electrons around the K^+ ion. This results in the attractive force between K^+ and Cl^- being weaker than that between Na^+ and Cl^-. This is supported by the lattice enthalpy for KCl (+701 kJ mol^{-1}) being smaller than that for NaCl (+771 kJ mol^{-1}).

2 NaF, NaBr and NaI

The cation is the same in all three compounds, but the anion gets steadily larger. This decreases the force of attraction between the ions, giving NaI the smallest lattice enthalpy of the three compounds: NaI < NaBr < NaF.

3 MgF_2 and NaF

The Mg^{2+} ion has a greater charge than Na^+ and, additionally, is a smaller ion than Na^+. Consequently the product of the ionic charges, q_1q_2, for MgF_2 is larger and the ionic radius is smaller than for NaF, giving a much greater force of attraction between the Mg^{2+} ion and the F^- ion. This is supported by the lattice enthalpy of MgF_2 (+2957 kJ mol^{-1}) being more than three times that of NaF (+902 kJ mol^{-1}).

Summary of effect of charge and radii on lattice enthalpy:

- **Increasing the charge on an ion increases the lattice enthalpy.**
- **Decreasing the ionic radius increases the lattice enthalphy.**

The smaller the ions and the larger their charge, the greater the lattice enthalpy of the ionic compound will be.

While Born–Haber cycles are used to determine lattice enthalpies from experimental results (experimental lattice enthalpy values), Coulomb's law is used to determine theoretical lattice enthalpy values for ionic compounds. These can be compared and conclusions drawn.

AS **15.2.4**
Discuss the difference between theoretical and experimental lattice enthalpy values of ionic compounds in terms of their covalent character. © IBO 2007

TABLE 4.2.2 COMPARISON OF EXPERIMENTAL AND THEORETICAL LATTICE ENTHALPIES FOR SOME IONIC COMPOUNDS

Compound	Lattice enthalpy (kJ mol^{-1}) Experimental	Theoretical	Discrepancy (%)	Compound	Lattice enthalpy (kJ mol^{-1}) Experimental	Theoretical	Discrepancy (%)
NaF	902	891	1.2	AgF	955	870	8.9
NaCl	771	766	0.6	AgCl	905	770	14.9
NaBr	733	732	0.1	AgBr	890	758	14.8
NaI	684	686	0.3	AgI	876	736	16.0

THEORY OF KNOWLEDGE

- How useful are theoretical values in the advancement of our knowledge of lattice enthalpies? How are these theoretical values obtained?
- What justification is used to account for discrepancies between the experimental and theoretical lattice enthalpy values for silver halides? Are these discrepancies due to experimental limitations or theoretical assumptions?

When experimental and theoretical lattice enthalpies are very similar (e.g. NaCl) , we can assume that the purely ionic model (spheres with charge evenly distributed) describes the compound accurately. The sodium halides have theoretical lattice enthalpies that are within 2% of the experimental values, showing that they closely resemble the theoretical model. In contrast, the theoretical lattice enthalpies of the silver halides are very different from their experimental values, with discrepancies of up to 16% in the case of AgI. This indicates that the theoretical model of separate spherical ions with evenly distributed charge does not accurately represent these compounds.

In each case, the experimental lattice enthalpy is larger than the theoretical lattice enthalpy, indicating some extra bonding between the ions. We can explain this in terms of the relative sizes of the ions and their interaction with each other. In the case of silver iodide, the silver ion is considerably smaller than the iodide ion (0.126 nm compared to 0.219 nm). The small positive silver ion is able to approach the iodide ion closely and to distort its electron cloud by attracting the electrons of the iodide ion towards itself. The iodide ion is particularly easy to distort because its valence electrons, in the 5th electron shell, are far from the nucleus. This distortion means that there are more electrons than expected between the silver and iodine nuclei. Such a concentration of electron density is commonly associated with covalent bonding, so we say that there is a greater degree of covalent character in AgI than NaCl. The degree of distortion of the iodide ion may lead it to being described as polarized.

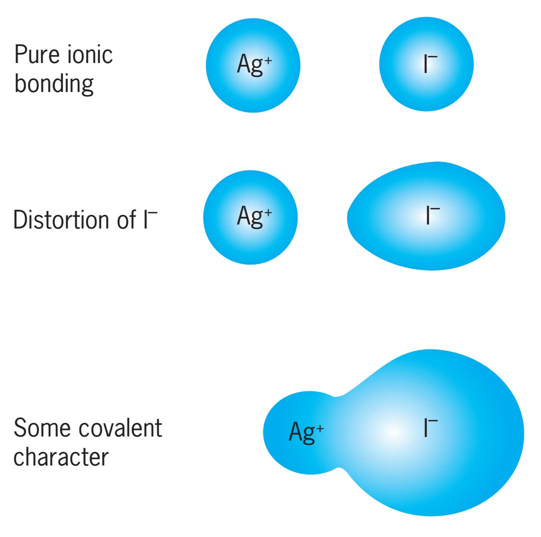


Figure 4.2.4 The small cation distorts the larger anion, creating a region of higher electron density between the two ions.

This increased covalent character in the case of AgI is supported by the small difference in electronegativity between silver and iodine (0.6 units) compared with the large difference between sodium and chlorine (2.1 units). Covalent bonds usually occur between atoms with similar electronegativities.

The degree of covalent character increases down the halogen group. The discrepancy between the experimental and theoretical values of lattice enthalpy for AgF is 8.9% while it is 16% for AgI. The discrepancy between the experimental values of lattice enthalpy is calculated as follows:

$$\%\ \text{discrepancy} = \frac{\text{experimental value} - \text{theoretical value}}{\text{experimental value} \times 100}$$

Positive ions that are small and highly charged (even with a 2+ charge) tend to produce greater **polarization** in the anion to which they are bonded than do larger cations with only a 1+ charge, since they are able to attract the electrons of the anion more strongly.

Covalent character increases down a group and across a period.

Covalent character increases as the difference between experimental and theoretical values of lattice enthalpy increases.

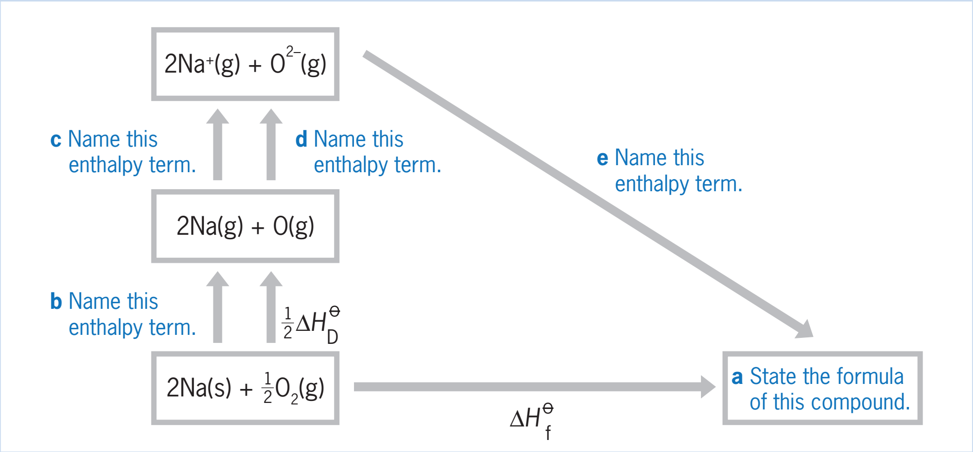
Section 4.2 Exercises

1 Distinguish between the terms *ionization energy* and *electron affinity*.

2 Write an equation to represent each of the following enthalpy terms.

- **a** Enthalpy of atomization of potassium
- **b** Enthalpy of dissociation of bromine gas
- **c** First ionization energy of potassium
- **d** First electron affinity of bromine
- **e** Enthalpy of formation of potassium bromide
- **f** Lattice enthalpy of potassium bromide

3 Complete the following Born–Haber cycle for sodium oxide.



4 The lattice enthalpy of rubidium chloride, RbCl, can be determined using a Born–Haber cycle.

Use the data in the table below to construct a Born–Haber cycle and determine a value for the lattice enthalpy of rubidium chloride.

Enthalpy change	Enthalpy (kJ mol^{-1})
Atomization of rubidium	+81
Atomization of chlorine	+244
First ionization energy of rubidium	+403
First electron affinity of chlorine	–349
Formation of rubidium chloride	–435

5 Explain why both the first and second ionization energies of calcium need to be included in the Born–Haber cycle for the determination of the lattice enthalpy of calcium chloride.

6 Consider each of the following pairs and explain which compound you would expect to have the greater lattice enthalpy.

- **a** KCl or KI
- **b** MgO or MgS
- **c** BaO or MgO

d LiF or CsF

e KCl or $CaCl_2$

7 Describe the assumption that is made in determining theoretical lattice enthalpy values.

8 Explain why the experimental lattice enthalpy for an ionic compound is generally greater than the theoretical lattice enthalpy.

9 Consider the following values of theoretical and experimental lattice enthalpies and then deduce the order of increasing covalent character for the following ionic compounds.

Compound	Theoretical lattice enthalpy (kJ mol^{-1})	Experimental lattice enthalpy (kJ mol^{-1})
Potassium fluoride	795	801
Calcium oxide	3477	3513
Lithium iodide	728	744
Silver bromide	758	890

10 Considering the theoretical and experimental lattice enthalpies shown in the table below, compare the bonding in sodium chloride and silver chloride.

Compound	Theoretical lattice enthalpy (kJ mol^{-1})	Experimental lattice enthalpy (kJ mol^{-1})
Sodium chloride	766	771
Silver chloride	770	905

4.3 ENTROPY

When a bottle of a volatile compound such as concentrated ammonia is opened, the smell is soon detected by students working well away from the open bottle. The ammonia vapours diffuse rapidly through the air. This is why we limit the opening of such bottles to a fume cupboard and recommend that the lid is replaced rapidly after use.

Diffusion is an excellent example of the natural tendency of systems to increase their mixing or disorder. Other examples include dissolving and changes of state such as evaporation and melting. These changes are **spontaneous** as they occur of their own accord.

The majority of spontaneous chemical reactions are exothermic reactions. Spontaneous redox reactions are a good example of this. The reaction between zinc and copper sulfate in a beaker releases heat energy, but if we separate the two in a voltaic cell we can harness the released energy as electrical energy. The evaporation and melting of water as well as many dissolving processes are endothermic, but these can be spontaneous because they involve the spreading out or disordering of the particles.

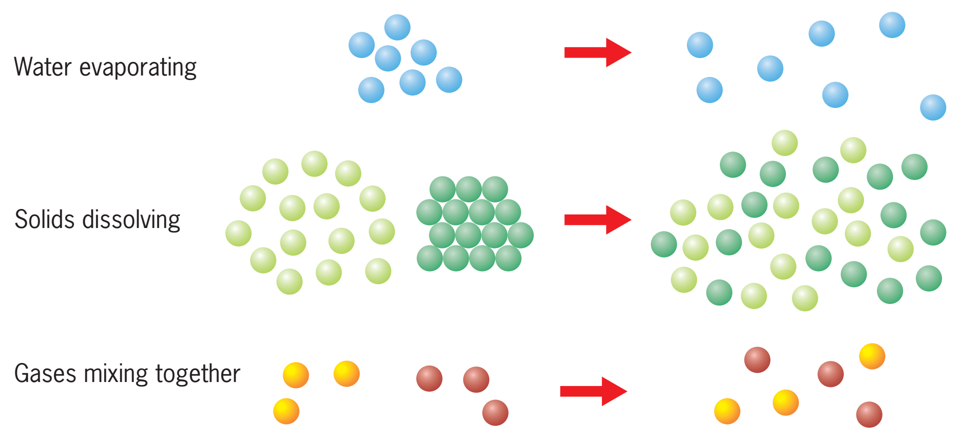


Figure 4.3.1 Evaporation, dissolving and diffusion of gases are all examples of spontaneous processes.

AS 15.3.1
State and explain the factors that increase the entropy in a system. © IBO 2007

Entropy, symbol S, is a term used for the randomness or disorder of a system. The second law of thermodynamics states that the entropy of an isolated system (when not in equilibrium) will tend to increase over time. Just as a student's bedroom starts off in a tidy state at the beginning of term and becomes more and more untidy as the term progresses, so too the entropy of a chemical system increases over time.

When gas particles diffuse, they are mixing with other gas particles and becoming more random, or disordered. The disorder of the solute particles increases when they are dissolved in a solution. Similarly the water molecules become more disordered as they spread apart from the solid to liquid state, or liquid to gaseous state. In each of these cases, the entropy increases.

An increase in disorder produces a positive ΔS value.

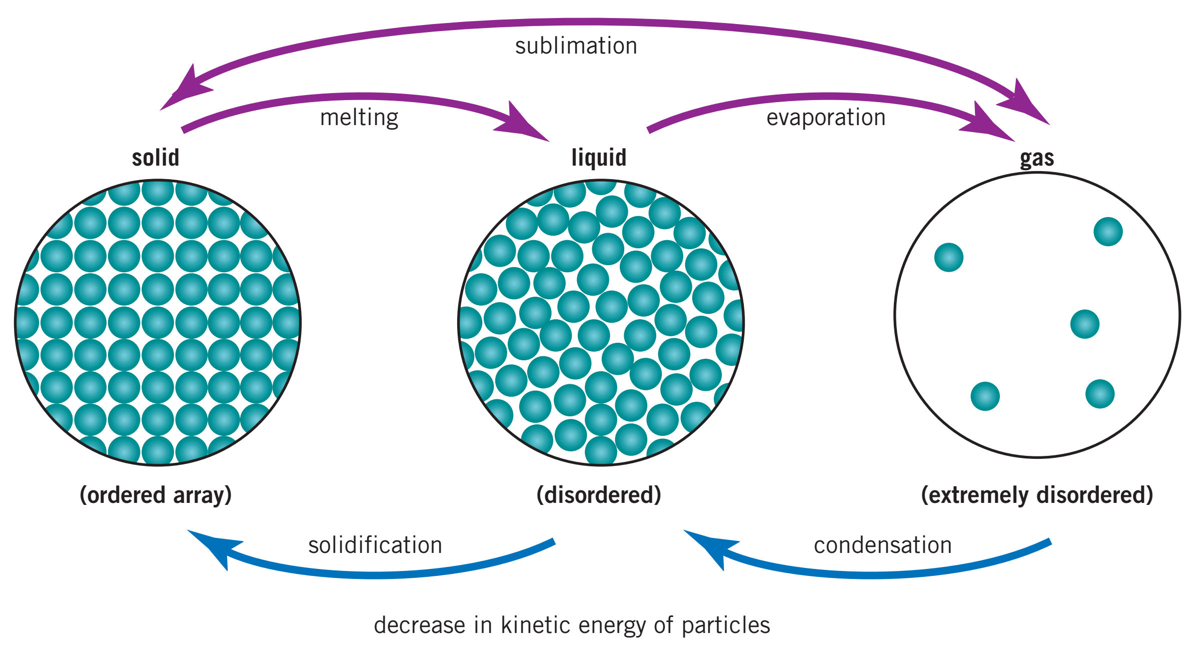


Figure 4.3.2 The degree of disorder increases from solid to liquid to gas.

Let us look specifically at some cases in which entropy increases.

1 The dissolution of ammonium nitrate

This is an endothermic reaction. The solid ammonium nitrate is a highly ordered arrangement of ammonium and nitrate ions in a lattice. When it dissolves, its ions become spread throughout the solution in a random arrangement.

$$NH_4NO_3(s) \xrightarrow{\text{water}} NH_4^+(aq) + NO_3^-(aq) \qquad \Delta H = +25 \text{ kJ mol}^{-1}$$

Examination of the equation for the reaction shows two particles on the right-hand side of the arrow for every one particle on the left-hand side of the arrow. This increase in the number of particles is a useful indicator of an increase in entropy.

2 Changes of state

Figure 4.3.3 An increase in entropy accompanies the sublimation of iodine.

When the state of a substance changes from solid to liquid or from liquid to gas, or even directly from solid to gas, as in the case of iodine, the arrangement of the particles becomes more disordered.

$$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +6.0 \text{ kJ mol}^{-1}$$
$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H = +44 \text{ kJ mol}^{-1}$$
$$I_2(s) \rightarrow I_2(g) \qquad \Delta H = +137 \text{ kJ mol}^{-1}$$

In all of the above equations the entropy of the system increases.

3 Decomposition

Decomposition of organic matter by bacteria as well as the thermal or spontaneous decomposition of a substance is accompanied by an increase in entropy.

$$(NH_4)_2CO_3(s) \rightarrow 2NH_3(g) + CO_2(g) + H_2O(g) \qquad \Delta H = +68 \text{ kJ mol}^{-1}$$

In the example of the decomposition of ammonium carbonate, one mole of ammonium carbonate decomposes to form four mole of gases. The increase in the number of mole of particles, together with the fact that they are gases whereas the reactant was a solid, makes this a clear example of an increase in entropy.

Figure 4.3.4 The decomposition of plant material produces gaseous methane, which in this case has been trapped in a frozen pond.

4 Increase in temperature

When the temperature of a system increases, the kinetic energy of the particles increases and they gain more freedom to move. Even if the state does not change, the entropy increases. All substances, for instance, have greater entropy at room temperature than at 0 K.

When you wish to predict the entropy change, ΔS, for a given reaction, it is important to note states of reactants and products, as well as the relative numbers of mole of reactants and products. The most useful question to ask yourself will be: Are there more gaseous product molecules than there were gaseous reactant molecules? If this is the case, the entropy will be positive.

AS 15.3.2
Predict whether the entropy change (ΔS) for a given reaction or process is positive or negative. © IBO 2007

Worked example 1

Consider each of the following reactions and determine which would have the most positive value of ΔS:

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

b $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

c $2Al(s) + 3S(s) \rightarrow Al_2S_3(s)$

d $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g)$

Solution

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

In this reaction there are 3 mol of gaseous reactants and 3 mol of gaseous products. ΔS would be almost, if not equal to, zero.

b $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

In this reaction there are 4 mol of gaseous reactants and 2 mol of gaseous product. ΔS would be negative; the entropy of the system has decreased.

c $2Al(s) + 3S(s) \rightarrow Al_2S_3(s)$

In this reaction there are no gaseous reactants or products. All reactants and products are solid and there are fewer product particles than reactant particles. ΔS would be negative; the entropy of the system has again decreased.

d $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g)$

In this reaction there are 2 mol of gaseous reactants and 4 mol of gaseous products. ΔS would be positive; the entropy of the system has increased.

AS 15.3.3
Calculate the standard entropy change for a reaction ($\Delta S^\ominus$) using standard entropy values ($S^\ominus$). © IBO 2007

Like enthalpy, entropy can be measured under standard conditions, so the standard entropy change for a reaction would have the symbol $\Delta S^\ominus$. Standard entropy is the absolute entropy of a substance at 1.01×10^2 kPa and 298 K. The units of entropy are J K^{-1} or J K^{-1} mol^{-1}. Entropy values are typically quite small, so joules rather than kilojoules are used.

The standard entropy change for a reaction is calculated in the same manner as standard enthalpy change for a reaction. Standard entropy values are used as given, or from data tables. Note that the standard entropies of elements and compounds are all positive, unlike standard enthalpies of formation for elements, which are equal to zero.

TABLE 4.3.1 STANDARD ENTROPY VALUES FOR SOME SUBSTANCES
(Some of these values can also be found in Appendix 3 and in table 11 of the IB data booklet. © IBO 2007)

Substance	Formula	State	$\Delta S^\ominus$ (J K^{-1} mol^{-1})	Substance	Formula	State	$\Delta S^\ominus$ (J K^{-1} mol^{-1})
Ammonia	NH_3	g	193	Methane	CH_4	g	186
Ammonium chloride	NH_4Cl	s	95	Methanol	CH_3OH	g	238
Butane	C_4H_{10}	g	310	Methanol	CH_3OH	l	127
But-1-ene	C_4H_8	g	307	Nitrogen	N_2	g	192
Carbon dioxide	CO_2	g	214	Nitrogen dioxide	NO_2	g	304
Chlorine	Cl_2	g	223	Oxygen	O_2	g	205
Chloroethane	C_2H_5Cl	g	276	Ozone	O_3	g	238
Dinitrogen tetroxide	N_2O_4	g	304	Pentane	C_5H_{12}	l	261
Ethane	C_2H_6	g	230	Propane	C_3H_8	g	270
Ethene	C_2H_4	g	219	Propene	C_3H_6	g	267
Ethyne	C_2H_2	g	201	Sulfur dioxide	SO_2	g	249
Hexane	C_6H_{14}	l	296	Sulfur trioxide	SO_3	g	256
Hydrogen	H_2	g	131	Water	H_2O	g	189
Hydrogen chloride	HCl	g	187	Water	H_2O	l	70

For a reaction

$$aA + bB \rightarrow cC + dD$$

standard entropy change of reaction $\Delta S^\ominus_{rxn}$ is given by

$$\begin{aligned}\Delta S^\ominus &= \sum\Delta S^\ominus(\text{products}) - \sum\Delta S^\ominus(\text{reactants})\\ &= [c\Delta S^\ominus(C) + d\Delta S^\ominus(D)] - [a\Delta S^\ominus(A) + b\Delta S^\ominus(B)]\end{aligned}$$

Worked example 2

Calculate the standard entropy change for the following reactions at 25°C.

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

b $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

c $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g)$

Solution

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

$$\begin{aligned}\Delta S^\ominus_{rxn} &= [S^\ominus(CO_2) + 2S^\ominus(H_2O(g))] - [S^\ominus(CH_4) + 2S^\ominus(O_2)] \\ &= [(1\text{ mol})(214\text{ J K}^{-1}\text{ mol}^{-1}) + (2\text{ mol})(189\text{ J K}^{-1}\text{ mol}^{-1}) \\ &\quad - [(1\text{ mol})(186\text{ J K}^{-1}\text{ mol}^{-1}) + (2\text{ mol})(205\text{ J K}^{-1}\text{ mol}^{-1})] \\ &= 592 - 596\text{ J K}^{-1} \\ &= -4\text{ J K}^{-1}\end{aligned}$$

As predicted in worked example 1 part **a**, this entropy change is very close to zero.

b $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

$$\begin{aligned}\Delta S^\ominus_{rxn} &= [S^\ominus(CH_3OH) + S^\ominus(H_2O(g))] - [S^\ominus(CO_2) + 3S^\ominus(H_2)] \\ &= [(1\text{ mol})(238\text{ J K}^{-1}\text{ mol}^{-1}) + (1\text{ mol})(189\text{ J K}^{-1}\text{ mol}^{-1}) \\ &\quad - [(1\text{ mol})(214\text{ J K}^{-1}\text{ mol}^{-1}) + (3\text{ mol})(131\text{ J K}^{-1}\text{ mol}^{-1})] \\ &= 427 - 607\text{ J K}^{-1} \\ &= -180\text{ J K}^{-1}\end{aligned}$$

There is a large decrease in entropy for this reaction, as could be predicted by the formation of 2 mol of products from 4 mol of reactants.

c $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO_2(g)$

$$\begin{aligned}\Delta S^\ominus_{rxn} &= [(3S^\ominus(H_2) + S^\ominus(CO_2(g))] - [S^\ominus(CH_4) + S^\ominus(H_2O)] \\ &= [(3\text{ mol})(131\text{ J K}^{-1}\text{ mol}^{-1}) + (1\text{ mol})(214\text{ J K}^{-1}\text{ mol}^{-1}) \\ &\quad - [(1\text{ mol})(186\text{ J K}^{-1}\text{ mol}^{-1}) + (1\text{ mol})(189\text{ J K}^{-1}\text{ mol}^{-1})] \\ &= 607 - 375\text{ J K}^{-1} \\ &= +232\text{ J K}^{-1}\end{aligned}$$

There is a large increase in entropy for this reaction as could be predicted by the formation of 4 mol of gaseous products from 2 mol of gaseous reactants.

Section 4.3 Exercises

1 Explain what is meant by the term *entropy*.

2 Explain why the entropy of a solid is less than the entropy of the gaseous form of the same substance.

3 Explain how a change in temperature may increase the entropy of a system.

4 Arrange the following in order of increasing entropy.

- **I** 1 mol $H_2O(l)$ at 100°C, 101.3 kPa
- **II** 1 mol $H_2O(s)$ at 0°C, 101.3 kPa
- **III** 1 mol $H_2O(l)$ at 0°C, 101.3 kPa
- **IV** 1 mol $H_2O(g)$ at 100°C, 101.3 kPa
- **V** 1 mol $H_2O(l)$ at 25°C, 101.3 kPa

5 For each reaction, state whether it has a positive or negative entropy change.

- **a** $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- **b** $N_2O_4(g) \rightarrow 2NO_2(g)$
- **c** $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
- **d** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- **e** $C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g)$

6 Arrange the following reactions in order of increasing entropy change.

- **I** $COCl_2(g) \rightarrow CO(g) + Cl_2(g)$
- **II** $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$
- **III** $C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$
- **IV** $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

7 Describe how the entropy of water changes as it condenses from steam to liquid water, and then use table 4.3.1 to calculate the entropy change for the reaction:
$H_2O(g) \rightarrow H_2O(l)$

8 Using table 4.3.1, calculate the standard entropy change for each of the following equations.

- **a** $C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g)$
- **b** $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$
- **c** $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
- **d** $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

THEORY OF KNOWLEDGE

In your study of Chemistry so far you have gained an understanding of the different ways in which scientific knowledge is produced, in other words, 'how scientists know', and you are learning about 'what chemists know' about the nature of matter. As learners we rarely stop to think about the process by which this happens, its limitations and strengths. Reflect on your experiences as a knower in Chemistry by considering the following.

- Give an example of chemical knowledge that has been simultaneously reliable and tentative. What are the advantages of both existing simultaneously?
- What makes the knowledge claims made by scientists more believable (e.g. consider the use of empirical evidence, inductive reasoning, dealing with uncertainty, reproducibility).
- What similarities and differences have you found in the method used to gain knowledge in the natural sciences compared to the method used in the human sciences?
- How do creativity, imagination and risk taking assist in the production of new knowledge? Support with specific examples.
- The process of science produces theories and laws. Distinguish between them and describe some of the characteristics of well-established scientific laws and theories.
- Why is it important for scientists from different countries and research organizations to collaborate and communicate with one another effectively during research? What is a peer review and why is it so important?
- Give some examples to illustrate how the social and cultural context of a scientist's work and their experience, age and expectations might affect the outcome of a scientific endeavour.
- Describe a story from the history of science that shows scientific knowledge being produced from evolutionary or gradual changes in what we know, and an example from a revolutionary or sudden change in thinking.
- Give an example to illustrate how the advancement of scientific knowledge has impacted and is dependent on the development of new technologies.
- What motivates scientists to do research?

4.4 SPONTANEITY

What is the driving force that makes a reaction spontaneous? Is it that heat energy is released as the reaction proceeds (an exothermic reaction) or perhaps that the system becomes more disordered as products are made (positive entropy)? Perhaps it is a combination of enthalpy and entropy?

Consider the reaction in which ammonia is produced.

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

$\Delta H^{\ominus}_{rxn} = \sum n\Delta H^{\ominus}_f(\text{products}) - \sum m\Delta H^{\ominus}_f(\text{reactants})$ (see section 4.1)

$\Delta H^{\ominus}_{rxn} = [(2\ \text{mol})(-46.3\ \text{kJ mol}^{-1})] - [(1\ \text{mol})(0\ \text{kJ mol}^{-1}) + (3\ \text{mol})(0\ \text{kJ mol}^{-1})]$
$= -92.6\ \text{kJ mol}^{-1}$ (i.e. the enthalpy change for the molar quantities in this reaction is –92.6 kJ)

The reaction is exothermic.

$\Delta S^{\ominus}_{rxn} = \sum n\Delta S^{\ominus}(\text{products}) - \sum m\Delta S^{\ominus}(\text{reactants})$ (see section 4.3)

$\Delta S^{\ominus}_{rxn} = [(2\ \text{mol})(193\ \text{J K}^{-1}\text{mol}^{-1})] - [(1\ \text{mol})(191.5\ \text{J K}^{-1}\text{mol}^{-1})$
$+ (3\ \text{mol})(131\ \text{J K}^{-1}\text{mol}^{-1})]$
$= 386 - 584.5$
$= -198.5\ \text{J K}^{-1}$

The entropy of the reaction is not favourable to a spontaneous reaction. This can be seen qualitatively by noticing that the reaction has 4 mol of gaseous reactants and 2 mol of gaseous products—a significant increase in order (decrease in disorder).

So in the case of such a well-known reaction, enthalpy and entropy disagree as to whether the reaction should go ahead.

Gibbs free energy, ***G***, reflects the balance between these two quantities. It may be described as the energy available to do work or more clearly as the 'driving force' (although it is not really a force) of a chemical reaction. It is calculated as a combination of the enthalpy and entropy of a reaction with the temperature at which the reaction is carried out also being considered.

$$\Delta G = \Delta H - T\Delta S$$

Gibbs free energy has two components: the change in enthalpy, ΔH, and the change in entropy, ΔS, which is combined with the temperature (in kelvin) at which the reaction is occurring.

- ΔH is the drive toward stability. When $\Delta H < 0$ the products are more stable (have a lower enthalpy) than the reactants.
- ΔS is the drive toward disorder. When $\Delta S > 0$, the products are more disordered than the reactants. Note that increasing T increases the influence of ΔS on the reaction's 'driving force.'
- Temperature is always quoted in kelvin for calculations of ΔG.

Gibbs free energy can be used to determine whether a reaction will go ahead on its own or not. That is, whether or not it is spontaneous. The change in Gibbs free energy is defined in the same way as the change in enthalpy, ΔH.

AS **15.4.1**
Predict whether a reaction or process will be spontaneous by using the sign of $\Delta G^{\ominus}$.
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$$\Delta G = G(\text{products}) - G(\text{reactants})$$

As for enthalpy and entropy, Gibbs free energy, $G^{\ominus}$, is usually quoted under standard conditions (298 K and 1.01×10^2 kPa pressure) and the standard free energy change is $\Delta G^{\ominus}$.

A negative value for $\Delta G^\ominus$ accompanies a spontaneous reaction, while a positive value means that the reaction is not spontaneous. Note that the value for ΔG° says nothing about the rate of the reaction. The reaction may proceed very slowly indeed, yet have a negative value of $\Delta G^\ominus$.

If $\Delta G^\ominus < 0$ the reaction is spontaneous.

If $\Delta G^\ominus = 0$ the reaction is at equilibrium.

If $\Delta G^\ominus > 0$ the reaction is not spontaneous.

AS 15.4.2 Calculate $\Delta G^\ominus$ for a reaction using the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ and by using values of the standard free energy change of formation, $\Delta G_f^\ominus$. © IBO 2007

For a chemical reaction $\Delta H^\ominus$ and $\Delta S^\ominus$ are independent of each other; that is, you cannot calculate one from the other. You can have situations where both are positive, both are negative, or one is positive and the other negative.

Notice that if ΔH and ΔS have the same sign they are working against each other, and the larger quantity will win. Entropy values are usually much smaller than enthalpy values and are quoted in joules rather than kilojoules. However, if the temperature is increased the entropy term ($T\Delta S$) may become greater than the enthalpy term. Similarly, as the temperature decreases, the entropy term becomes less significant and the enthalpy term dominates.

Under what circumstances might ΔG be negative?

1 In an exothermic reaction with an increase in entropy

$\Delta H^\ominus$ is negative, so if $\Delta S^\ominus$ is positive, then

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= (\text{negative}) - (\text{positive}) = \text{negative}\end{aligned}$$

The reaction will be spontaneous, no matter what the temperature.

Worked example 1

For the following reaction, $\Delta H^\ominus$ is negative and $\Delta S^\ominus$ is positive:

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

Determine whether the reaction will be spontaneous at room temperature.

Solution

There is no need to actually calculate $\Delta G^\ominus$.

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= (\text{negative}) - (\text{positive}) = \text{negative}\end{aligned}$$

This reaction will be spontaneous at any temperature. However, we cannot make any assumptions about the rate of the reaction. You may recognize this decomposition of hydrogen peroxide as one that requires a catalyst to proceed at a measurable rate.

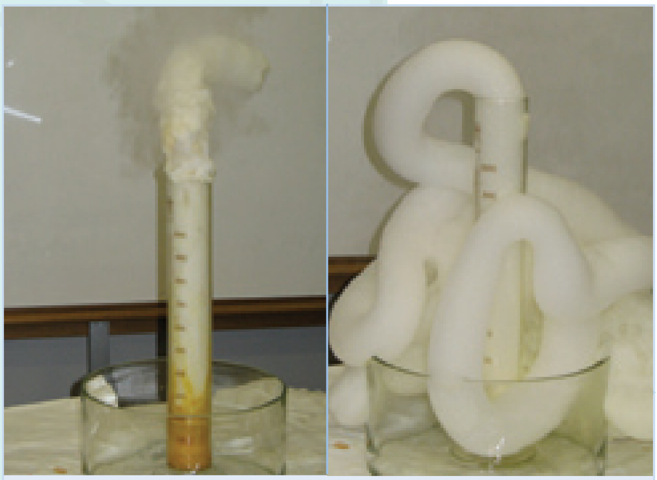


Figure 4.4.1 While it is a spontaneous reaction, the rate of the decomposition of hydrogen peroxide is very slow unless a catalyst such as potassium iodide is used to increase the rate of reaction.

2 In an exothermic reaction with a decrease in entropy being carried out at a low temperature

$\Delta H^\ominus$ is negative and $\Delta S^\ominus$ is negative, therefore $\Delta G^\ominus$ will only be negative if $T\Delta S^\ominus$ has a negative value that is smaller than the value of $\Delta H^\ominus$.

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= \text{(negative)} - \text{(smaller negative)} = \text{negative}\end{aligned}$$

The reaction will be spontaneous only at low temperatures. The actual temperatures depend upon the relative sizes of $\Delta H^\ominus$ and $\Delta S^\ominus$.

Worked example 2

For the following example find $\Delta H^\ominus$ and $\Delta S^\ominus$, then determine the highest temperature at which the reaction will be spontaneous.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

Solution

$$\begin{aligned}\Delta H^\ominus_{rxn} &= \Sigma n\Delta H^\ominus_f(\text{products}) - \Sigma m\Delta H^\ominus_f(\text{reactants}) \\ &= [(1\text{ mol})(\Delta H^\ominus_f(NH_4Cl)] - [(1\text{ mol})(\Delta H^\ominus_f(NH_3) + (1\text{ mol})(\Delta H^\ominus_f(HCl)] \\ &= [(1\text{ mol})(-315.4\text{ kJ mol}^{-1})] - [(1\text{ mol})(-46.3\text{ kJ mol}^{-1}) \\ &\quad + (1\text{ mol})(-92.3\text{ kJ mol}^{-1})] \\ &= -315.4 - (-138.6) \\ &= -176.8\text{ kJ mol}^{-1}\end{aligned}$$

The reaction is exothermic.

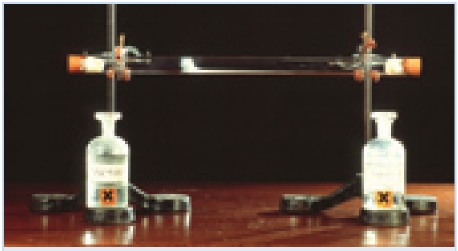


Figure 4.4.2 The formation of ammonium chloride is clearly demonstrated when cotton wool balls soaked in HCl and NH_3 are placed at either end of a tube and the vapours diffuse towards each other.

$$\begin{aligned}\Delta S^\ominus_{rxn} &= \Sigma n\Delta S^\ominus(\text{products}) - \Sigma m\Delta S^\ominus(\text{reactants}) \text{ (see section 4.3)} \\ &= [(1\text{ mol})(\Delta S^\ominus(NH_4Cl)] - [(1\text{ mol})(\Delta S^\ominus(NH_3) + (1\text{ mol})(\Delta S^\ominus(HCl)] \\ &= [(1\text{ mol})(95\text{ J K}^{-1}\text{mol}^{-1})] - [(1\text{ mol})(193\text{ J K}^{-1}\text{mol}^{-1}) \\ &\quad + (1\text{ mol})\,(187\text{ J K}^{-1}\text{mol}^{-1})] \\ &= 94.6 - 380 \\ &= -285\text{ J K}^{-1}\end{aligned}$$

The entropy of the reaction is not favourable to a spontaneous reaction. This can be seen qualitatively by noticing that the reaction has 2 mol of gaseous reactants and 1 mol of solid products—an increase in order (decrease in disorder).

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$$

To find the temperature at which the reaction ceases to be spontaneous, substitute $\Delta G^\ominus = 0$ as this is the greatest value at which the reaction is not spontaneous.

$$\begin{aligned}0 &= -176\,800 - T \times -285 \\ T \times -285 &= -176\,800 \\ T &= \frac{-176\,800}{-285} \\ &= 620\text{ K}\end{aligned}$$

Note that units of $\Delta H^\ominus$ have been changed to J (multiplied by 1000) to agree with units of $\Delta S^\ominus$.

The reaction is spontaneous at temperatures below 620 K (347°C).

3 In an endothermic reaction with an increase in entropy at high temperatures.

$\Delta H^\ominus$ is positive, therefore $\Delta G^\ominus$ will be negative only if $T\Delta S^\ominus$ has a positive value that is larger than the value of $\Delta H^\ominus$.

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= \text{(positive)} - \text{(larger positive)} = \text{negative}\end{aligned}$$

The reaction will be spontaneous only at high temperatures.

Under what circumstances might ΔG be positive?

1 In an endothermic reaction with a decrease in entropy

$\Delta H^\ominus$ is positive, therefore if $\Delta S^\ominus$ is negative $\Delta G^\ominus$ will always be positive.

$$\begin{aligned}\Delta G^\ominus &= \Delta H^\ominus - T\Delta S^\ominus \\ &= \text{(positive)} - \text{(negative)} = \text{positive}\end{aligned}$$

The reaction will never be spontaneous.

Worked example 3

Explain why oxygen gas does not change spontaneously into ozone, $O_3(g)$, at room temperature (298 K).

$$3O_2(g) \rightarrow 2O_3(g)$$

Solution

$$\begin{aligned}\Delta H^\ominus_{rxn} &= \sum n\Delta H^\ominus_f(\text{products}) - \sum m\Delta H^\ominus_f(\text{reactants}) \\ &= [(2\ \text{mol})(\Delta H^\ominus_f(O_3)] - [(3\ \text{mol})(\Delta H^\ominus_f(O_2)] \\ &= [(2\ \text{mol})(+142.2\ \text{kJ mol}^{-1})] - [(3\ \text{mol})(0\ \text{kJ mol}^{-1})] \\ &= +284.4\ \text{kJ mol}^{-1} = 2.844 \times 10^5\ \text{J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\ominus_{rxn} &= \sum n\Delta S^\ominus(\text{products}) - \sum m\Delta S^\ominus(\text{reactants}) \\ &= [(2\ \text{mol})(237.6\ \text{J K}^{-1}\ \text{mol}^{-1})] - [(3\ \text{mol})(205.0\ \text{J K}^{-1}\ \text{mol}^{-1})] \\ &= 475.2 - 615.0 \\ &= -139.8\ \text{J K}^{-1}\end{aligned}$$

Since $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$$\begin{aligned}\Delta G^\ominus &= +2.844 \times 10^5 - (298 \times -139.8) \\ &= +2.844 \times 10^5 - (-4.17 \times 10^4) \\ &= 3.26 \times 10^5\ \text{J mol}^{-1} = +326\ \text{kJ mol}^{-1}\end{aligned}$$

The Gibbs free energy for this reaction is a large positive value, so oxygen gas will not change spontaneously into ozone at room temperature.

Note that the subtraction of a negative number from a positive number will always result in a positive value, so not only is this reaction not spontaneous at room temperature, it will never be spontaneous.

2 In an exothermic reaction

$\Delta H^{\ominus}$ is negative, therefore if $\Delta S^{\ominus}$ is negative and the temperature is high, then $T\Delta S^{\ominus}$ may have a larger negative value than $\Delta H^{\ominus}$ and $\Delta G^{\ominus}$ will be positive.

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus}\\ &= \text{(negative)} - \text{(larger negative)} = \text{positive}\end{aligned}$$

The reaction will not be spontaneous at high temperatures.

Worked example 4

Find the maximum temperature at which this reaction is spontaneous.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
$\Delta H^{\ominus} = -92.6\ \text{kJ mol}^{-1} = -9.26 \times 10^4\ \text{J}$
$\Delta S^{\ominus} = -198.5\ \text{J K}^{-1}$

Solution

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

A value of $\Delta G^{\ominus} = 0$ is the greatest value at which the reaction is not spontaneous.

$0 = -9.26 \times 10^4 - T \times -198.5$

$$T = \frac{-92\,600}{-198.5} = 466\ \text{K}$$

The reaction is spontaneous at temperatures up to 466 K (193°C).

3 In an endothermic reaction with an increase in entropy at low temperatures

$\Delta H^{\ominus}$ is positive, therefore $\Delta G^{\ominus}$ will be positive if $T\Delta S^{\ominus}$ has a positive value that is smaller than the value of $\Delta H^{\ominus}$.

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus}\\ &= \text{(positive)} - \text{(smaller positive)} = \text{positive}\end{aligned}$$

The reaction will not be spontaneous at low temperatures.

Worked example 5

$NH_4NO_3(s) \xrightarrow{\text{water}} NH_4^{+}(aq) + NO_3^{-}(aq)$

Find the minimum temperature at which this reaction will be spontaneous.

$\Delta H^{\ominus} = +28.05\ \text{kJ mol}^{-1} = +2.805 \times 10^4\ \text{J}$
$\Delta S^{\ominus} = 108.7\ \text{J K}^{-1}$

Solution

$\Delta G^{\ominus} = \Delta H^{-} - T\Delta S^{\ominus}$
A value of $\Delta G^{\ominus} = 0$ is the lowest value at which the reaction is spontaneous.
$0 = +2.805 \times 10^4 - T \times 108.7$
$T = 258\ \text{K}$

In theory this reaction will be spontaneous down to a temperature of 258 K (–15°C); however, it involves dissolution in water, whch would be very difficult below 0°C as the water would be frozen!

TABLE 4.4.1 SUMMARY OF EFFECTS OF SIGNS OF $\Delta H^\ominus$ AND $\Delta S^\ominus$ ON $\Delta G^\ominus$

		$\Delta H^\ominus$	
		Positive (+)	**Negative (–)**
$\Delta S^\ominus$	**Positive (+)**	$\Delta G^\ominus$ is negative at high temperatures and positive at low temperatures. e.g. $H_2(g) + I_2(g) \rightarrow 2HI(g)$	$\Delta G^\ominus$ is always negative. These reactions are always spontaneous. e.g. $2H_2O_2(l) \rightarrow 2H_2O(g) + O_2(g)$
	Negative (–)	$\Delta G^\ominus$ is always positive. These reactions are never spontaneous. e.g. $3O_2(g) \rightarrow 2O_3(g)$	$\Delta G^\ominus$ is positive at high temperatures and negative at low temperatures. e.g. $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

The standard Gibbs free energy of a reaction can also be calculated from tabulated values of standard free energies of formation, if these are available. Note that, as for standard enthalpies of formation, the **standard free energy change of formation** of any element in its most stable state is equal to zero. The same method of calculation is applied for **standard free energy change of reaction** as was used for calculating standard enthalpy of reaction and standard entropy of reaction.

$$\Delta G^\ominus_{rxn} = \Sigma n\Delta G^\ominus_f(\text{products}) - \Sigma m\Delta G^\ominus_f(\text{reactants})$$

TABLE 4.4.2 SOME VALUES OF ΔG

(Some of these values can also be found in Appendix 3 and in table 11 of the IB Data booklet. © IBO 2007)

Substance	Formula	State	$\Delta G^\ominus_f$ (kJ mol^{-1})	Substance	Formula	State	$\Delta G^\ominus_f$ (kJ mol^{-1})
Ammonia	NH_3	g	–17	Methane	CH_4	g	–51
Ammonium chloride	NH_4Cl	s	–204	Methanol	CH_3OH	l	–166
Butane	C_4H_{10}	g	–16	Nitrogen	N_2	g	0
But-1-ene	C_4H_8	g	72	Nitrogen dioxide	NO_2	g	52
Carbon dioxide	CO_2	g	–394	Nitrogen monoxide	NO	g	87
Chlorine	Cl_2	g	0	Oxygen	O_2	g	0
Ethane	C_2H_6	g	–33	Ozone	O_3	g	16
Ethene	C_2H_4	g	68	Propane	C_3H_8	g	–24
Ethanol	C_2H_5OH	g	–169	Propene	C_3H_6	g	63
Ethanol	C_2H_5OH	l	–175	Tetrachloromethane	CCl_4	g	–65
Ethyne	C_2H_2	g	209	Water	H_2O	g	–229
Hydrogen	H_2	g	0	Water	H_2O	l	–237
Hydrogen chloride	HCl	g	–95				

Worked example 6

Determine the standard Gibbs free energy of the following reaction.

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

Solution

$$\begin{aligned}\Delta G^{\ominus}_{\text{rxn}} &= \Sigma n\Delta G^{\ominus}_{\text{f}}(\text{products}) - \Sigma m\Delta G^{\ominus}_{\text{f}}(\text{reactants})\\ &= [(4\text{ mol})(\Delta G^{\ominus}_{\text{f}}(CO_2) + (6\text{ mol})(\Delta G^{\ominus}_{\text{f}}(H_2O)] - [(2\text{ mol})(\Delta G^{\ominus}_{\text{f}}(C_2H_6)\\ &\quad + (7\text{ mol})(\Delta G^{\ominus}_{\text{f}}(O_2)]\\ &= [(4\text{ mol})(-394\text{ kJ mol}^{-1}) + (6\text{ mol})(-229\text{ kJ mol}^{-1})]\\ &\quad - [(2\text{ mol})\ (-33\text{ kJ mol}^{-1}) + (7\text{ mol})(0\text{ kJ mol}^{-1})]\\ &= [(-1576) + (-1374)] - [-66]\\ &= -2884\text{ kJ mol}^{-1}\end{aligned}$$

This reaction is spontaneous under standard conditions.

The effect of a change in temperature on spontaneity

15.4.3
Predict the effect of a change in temperature on the spontaneity of a reaction using standard entropy and enthalpy changes and the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$. © IBO 2007

WORKSHEET 4.2
Energetics calculations

Consider worked example 4 (p. 117) in which the spontaneity of the reaction to form ammonia was determined.

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

$\Delta H^{\ominus} = -92.6\text{ kJ mol}^{-1} = -9.26 \times 10^4\text{ J}$
$\Delta S^{\ominus} = -198.5\text{ J K}^{-1}$

At 273 K:

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus}\\ &= -9.26 \times 10^4 - (273 \times -198.5)\\ &= -9.26 \times 10^4 - (-54\,190.5)\\ &= -3.84 \times 10^4\text{ J mol}^{-1}\\ &= -38.4\text{ kJ mol}^{-1}\end{aligned}$$

The reaction is spontaneous at 273 K (0°C).

As the temperature increases, $T\Delta S^{\ominus}$ becomes a larger negative number. When this eventually becomes greater than –92 600, $\Delta G^{\ominus}$ will become positive and the reaction will no longer be spontaneous. The temperature at which this occurs was determined in worked example 4. We can test this by finding the value of $\Delta G^{\ominus}$ at 500 K. It should be positive.

$$\begin{aligned}\Delta G^{\ominus} &= \Delta H^{\ominus} - T\Delta S^{\ominus}\\ &= -92\,600 - (500 \times -198.5)\\ &= -92\,600 - (-99\,250)\\ &= +\,6650\text{ J mol}^{-1}\\ &= +\,6.65\text{ kJ mol}^{-1}\end{aligned}$$

As expected, the standard Gibbs free energy is positive, so the reaction would not be spontaneo us at 500 K.

Section 4.4 Exercises

1 Explain what is meant by the term *Gibbs free energy*.

2 Describe how the sign of $\Delta G^{\ominus}$ relates to the spontaneity of a reaction.

3 Predict whether ΔG will positive or negative (or dependent on temperature) for a reaction that is:

- **a** endothermic and accompanied by a decrease in entropy over the reaction
- **b** endothermic and accompanied by a increase in entropy over the reaction
- **c** exothermic and accompanied by a decrease in entropy over the reaction
- **d** exothermic and accompanied by a increase in entropy over the reaction

CHEM COMPLEMENT

Free energy and equilibrium constants

While a reaction may start with reactants in their standard state (solutions with a concentration of 1 mol dm^{-3}), as soon as some reactants have formed products this will no longer be the case. ΔG rather than $\Delta G^\ominus$ should then be used to predict the progress of the reaction.

ΔG is related to $\Delta G^\ominus$ by the equation:

$$\Delta G = \Delta G^\ominus + RT\ln Q$$

where R is the gas constant, T is the temperature in kelvin and Q is the reaction quotient which reflects the ratio of products to reactants (see Chapter 6 'Equilibrium').

At a given temperature $\Delta G^\ominus$ is fixed, but ΔG may have a range of values depending on the value of Q.

At equilibrium, $\Delta G = 0$ and $Q = K$ where K is the equilibrium constant, so:

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

The larger the value of K (position of equilibrium lying far to the right), the more negative the value of $\Delta G^\ominus$ will be (a spontaneous reaction). Similarly, a non-spontaneous reaction with a positive value of $\Delta G^\ominus$ will have an equilibrium constant that is very small (position of equilibrium lies to the left-hand side). If the equilibrium constant = 1, then products and reactants are equally favoured and $\Delta G^\ominus = 0$.

4 **a** Using the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ given below, predict which of reactions A or B would be spontaneous at 298 K.

Reaction	$\Delta H^\ominus$ (kJ mol^{-1})	$\Delta S^\ominus$ (J K^{-1})
A	12.0	30
B	2.0	−110

b If either of the reactions is not spontaneous at 298 K, calculate whether it will be spontaneous at 498 K.

5 Using your answer to question **5** in the section 4.1 exercises and question **8d** in the section 4.3 exercises, calculate the standard free energy change, $\Delta G^\ominus$, at 100°C for the reaction

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

6 Using the data below, calculate the change in standard free energy at 250 K and 850 K for this reaction:

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$

Substance	$\Delta H^\ominus$ (kJ mol^{-1})	$\Delta S^\ominus$ (J K^{-1})
$Fe_2O_3(s)$	−822	90.0
$H_2(g)$	0	131
Fe(s)	0	27.0
$H_2O(g)$	−242	189

7 The following reaction is only spontaneous at 'high' temperatures:

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

If $\Delta H^\ominus = +180.8$ kJ mol^{-1} and $\Delta S^\ominus = +24.7$ J K^{-1} deduce the temperature at which the reaction begins to be spontaneous.

8 Using data from tables 4.1.1 and 4.3.1, calculate the temperature at which the transformation of $H_2O(l)$ to $H_2O(g)$ is spontaneous.

9 Using values in table 4.4.2, calculate the standard free energy of reaction for the following reactions.

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

b $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

c $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(g) + 4HCl(g)$

10 Calculate $\Delta G^\ominus{}_{rxn}$, using values for the standard free energy of formation, and compare the answer with that calculated using $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ for the reaction $N_2(g) + O_2(g) \rightarrow 2NO(g)$ at 298 K. ($\Delta H^\ominus = +180.8$ kJ mol^{-1} and $\Delta S^\ominus = +24.7$ J K^{-1})

Chapter 4 Summary

Terms and definitions

Electron affinity The energy change that occurs when an electron is accepted by an atom in the gaseous state to form a negative ion.

Enthalpy, H Heat energy

Entropy, S The randomness or disorder of a system.

Gibbs free energy, $\Delta G^{\ominus}$ The energy available to do useful work. It is defined in terms of enthalpy change and entropy change: $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

Lattice enthalpy The energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

Polarization The attraction of the valence electrons of an ion (or atom) to one region of the ion, creating a region of higher electron density.

Spontaneous Changes or reactions that take place of their own accord.

Standard enthalpy change of combustion, $\Delta H^{\ominus}_{c}$ The enthalpy change that occurs when one mole of a compound reacts with oxygen in the standard state.

Standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$ The enthalpy change that occurs when one mole of a compound is formed from its elements in their standard state.

Standard enthalpy change of reaction, $\Delta H^{\ominus}_{\text{rxn}}$ The enthalpy change that occurs when reactants are converted to products in their standard state.

Standard entropy change of reaction, $\Delta S^{\ominus}_{\text{rxn}}$ The change in the degree of disorder that occurs when reactants are converted to products in their standard state.

Standard free energy change of formation, $\Delta G^{\ominus}_{f}$ The free energy change that occurs when one mole of a compound is formed from its elements in their standard state.

Standard free energy change of reaction, $\Delta G^{\ominus}_{\text{rxn}}$ The free energy change when reactants are converted to products in their standard state.

Standard state The state in which a substance exists at 298 K and 1.01×10^{2} kPa.

Concepts

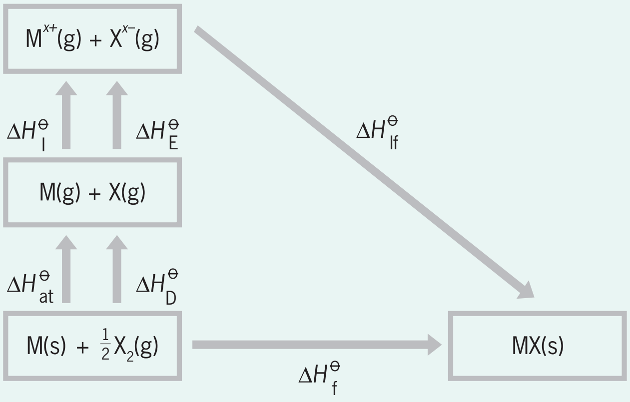
- The standard enthalpy change of formation, $\Delta H^{\ominus}_{f}$ of a compound is defined as the enthalpy change that results when one mole of a compound is formed from its elements at a pressure of 1.01×10^{2} kPa and 298 K.
- $\Delta H^{\ominus}_{f}$ of any element is defined as 0 kJ mol^{-1}.
- $\Delta H^{\ominus}_{f}$ values are tabulated and can be used to determine the standard enthalpy change of reaction, $\Delta H^{\ominus}_{\text{rxn}}$, for a given reaction.
- For a general reaction: $aA + bB \rightarrow cC + dD$

  $$\begin{aligned}\Delta H^{\ominus}_{\text{rxn}} &= [c\Delta H^{\ominus}_{f}(C) + d\Delta H^{\ominus}_{f}(D)] - [a\Delta H^{\ominus}_{f}(A) \\ &\quad + b\Delta H^{\ominus}_{f}(B)] \\ &= \Sigma n\Delta H^{\ominus}_{f}(\text{products}) - \Sigma m\Delta H^{\ominus}_{f}(\text{reactants}),\end{aligned}$$

  where Σ (sigma) means 'the sum of', and m and n represent the stoichiometric coefficients for the reactants and products.
- Similarly for a combustion reaction $aA + bO_2 \rightarrow cCO_2 + dH_2O$:

  $$\begin{aligned}\Delta H^{\ominus}_{c} &= \Sigma n\Delta G^{\ominus}_{f}(\text{products}) - \Sigma m\Delta G^{\ominus}_{f}(\text{reactants}) \\ &= [c\Delta H^{\ominus}_{f}(CO_2) + d\Delta H^{\ominus}_{f}(H_2O)] - [a\Delta H^{\ominus}_{f}(A) \\ &\quad + b\Delta H^{\ominus}_{f}(O_2)]\end{aligned}$$

  where A is the fuel.
- The lattice enthalpy of an ionic compound increases as the charge on the ions increase and as the size of the ions decreases.
- A Born–Haber cycle is made up of six enthalpy terms.



  - The enthalpy of formation, $\Delta H^{\ominus}_{f}$, is the sum of all of the other terms.
  - The lattice enthalpy, $\Delta H^{\ominus}_{L}$, has the same magnitude but opposite sign to the enthalpy of lattice formation, $\Delta H^{\ominus}_{lf}$, of the ionic compound.

- The larger the percentage difference between the experimentally determined value and the theoretical value of the lattice enthalpy, the greater the degree of covalent character in the bond.
- Entropy increases when:
  - a substance is heated
  - the particles are allowed to move more freely
  - a substance melts
  - a substance vaporizes
  - more mole of particles are present as products than as reactants.
- An increase in entropy (positive ΔS) represents an increase in disorder of the system.
- The standard entropy change for a reaction is calculated as

  $\Delta S = \Sigma\Delta S^{\ominus}(\text{products}) - \Sigma\Delta S^{\ominus}(\text{reactants})$
- The change in Gibbs free energy determines the spontaneity of a reaction.
  - If $\Delta G < 0$, the reaction is spontaneous.
  - If $\Delta G = 0$, the reaction is at equilibrium.
  - If $\Delta G > 0$, the reaction is not spontaneous.
- The Gibbs free energy change may be calculated using the equation $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
- The standard free energy change of a reaction may also be calculated from standard free energies of formation:
  $\Delta G^{\ominus}_{\text{rxn}} = \Sigma\Delta G^{\ominus}_{\text{f}}(\text{products}) - \Sigma\Delta G^{\ominus}_{\text{f}}(\text{reactants})$
- Reactions involving a positive enthalpy and a positive entropy or a negative enthalpy and a negative entropy are temperature dependent for their spontaneity.

		ΔH	
		+ve	**−ve**
ΔS^{o}	**+ve**	High temp: $\Delta G^{\ominus}$ −ve Low temp: $\Delta G^{\ominus}$ +ve	$\Delta G^{\ominus}$ is always −ve
	−ve	$\Delta G^{\ominus}$ is always +ve.	High temp: $\Delta G^{\ominus}$ +ve Low temp: $\Delta G^{\ominus}$ −ve

Chapter 4 Review questions

1 Make a summary table that shows the significance of positive and negative values for ΔH, ΔS and ΔG.

2 Explain the use of the symbols '$\ominus$' and '$_{\text{f}}$' in $\Delta H^{\ominus}_{\text{f}}$, $\Delta S^{\ominus}_{\text{f}}$ and $\Delta G^{\ominus}_{\text{f}}$.

3 Distinguish between the terms *standard enthalpy change of formation* and *standard enthalpy change of combustion*.

4 Write an equation for the formation of nitric acid that illustrates the definition of the standard enthalpy of formation.

5 **a** Write a balanced equation for the combustion of benzene, C_6H_6.

b The standard enthalpy change of combustion of benzene is –3267 kJ mol^{-1}. Using values in table 4.1.1, calculate the standard enthalpy change of formation of benzene.

6 Use the values in table 4.1.1 to calculate the standard enthalpy change of combustion of butane, C_4H_{10}.

7 Compare the following ionic compounds and state which one you would expect to have the greatest lattice enthalpy. You should explain the reason for your choice.

A $MgCl_2$

B NaCl

C MgO

8 The lattice enthalpy of an ionic compound can be calculated using a Born–Haber cycle. The following enthalpies are available for lithium fluoride:

$\Delta H^{\ominus}_{\text{L}}(\text{Li}) = +155.2\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{\text{D}}(\text{F}_2) = +158\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{\text{f}}(\text{Li}) = +520\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{\text{E}}(\text{F}) = -328\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{\text{f}}(\text{LiF}) = -594.1\ \text{kJ mol}^{-1}$
$\Delta H^{\ominus}_{\text{lf}}(\text{LiF}) = ?$

Construct a Born–Haber cycle for the formation of LiF and use the above enthalpy values to determine the standard enthalpy of lattice formation: $\text{Li}^{+}(\text{g}) + \text{F}^{-}(\text{g}) \rightarrow \text{LiF(s)}$. Use your answer to deduce the lattice enthalpy of LiF.

9 Describe how lattice enthalpies can be used to determine how closely the bonding in an ionic compound matches the ideal model of an ionic compound composed of spherical ions with their charge distributed evenly across the surface.

10 Considering the theoretical and experimental lattice enthalpies shown in the table below, compare the bonding in calcium fluoride and silver fluoride, and explain which compound most closely matches the ideal model of an ionic compound.

Compound	Theoretical lattice enthalpy (kJ mol^{-1})	Experimental lattice enthalpy (kJ mol^{-1})
Strontium oxide	3205	3310
Silver fluoride	870	955

11 Write the equations for the combustion of propane, butane and pentane, and predict which reaction will have the greatest increase in entropy.

12 Using an example to illustrate your answer, explain why decomposition reactions are typically accompanied by an increase in entropy.

13 **a** Write the equation for the dissolution of ammonium chloride in water.

b Use the equation you have written in part **a** to predict how the entropy will change in this reaction, giving a reason for your answer.

14 Using data from table 4.3.1, calculate the standard entropy change for the substitution reaction between ethane and chlorine:
$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$

15 Determine whether your prediction was accurate in question **11** by calculating the standard entropy change for the combustion of propane, butane and pentane.

16 Explain why a reaction with a negative value of $\Delta H^\ominus$ and a negative value of $\Delta S^\ominus$ is spontaneous only at low temperatures.

17 The following reaction is carried out at 25°C and 1.01×10^2 kPa pressure.

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

Using the data in the table below, calculate $\Delta H^\ominus$, $\Delta S^\ominus$ and $\Delta G^\ominus$ for this reaction.

Substance	$\Delta H^\ominus_f$ (kJ mol–1)	$\Delta S^\ominus$ (J $K^{-1}mol^{-1}$)
$SO_3(g)$	–396	256
$H_2O(l)$	–286	70
$H_2SO_4(l)$	–814	157

18 Ethyne reacts with hydrogen as follows:

$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

Use Appendix 3 to find $\Delta H^\ominus_{rxn}$ and $\Delta S^\ominus$ and hence calculate $\Delta G^\ominus$ for this reaction.

19 The addition reaction between steam and ethene produces ethanol.

a Write the equation for this reaction

b Use standard free energy values from table 4.4.2 to calculate $\Delta G^\ominus$ for this reaction at 273 K.

20 The following reaction occurs between hydrogen and iodine:

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

a Predict the change in entropy of this reaction.

b Using the following data, calculate $\Delta H^\ominus_{rxn}$ and $\Delta S^\ominus_{rxn}$.

Substance	$\Delta H^\ominus_f$ (kJ mol^{-1})	$\Delta S^\ominus_f$ (J $K^{-1}mol^{-1}$)
$H_2(g)$	0	+131
$I_2(g)$	0	+261
HI(g)	+25.9	206.3

c Determine the lowest temperature for which this reaction would be spontaneous.

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Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 4 Test

Part A: Multiple-choice questions

1 Consider the following information.

Compound	$C_6H_6(l)$	$CO_2(g)$	$H_2O(l)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	+49	−394	−286

$C_6H_6(l) + 7\frac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

Which expression gives the correct value of the standard enthalpy change of combustion for benzene(l), in kJ mol^{-1}?

A 12(−394) + 6(−286)−2(49)

B 12(394) + 6(286) −2(−49)

C 6(−394) + 3(−286) − (49)

D 6(394) + 3(286) − (−49)

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2 Which equation represents the lattice enthalpy of magnesium oxide?

A $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

B $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(g)$

C $Mg^{2+}(g) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

D $Mg^{2+}(g) + O^{2-}(g) \rightarrow MgO(s)$

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3 Which equation represents a change with a negative value for ΔS?

A $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

B $H_2O(s) \rightarrow H_2O(g)$

C $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

D $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

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4 Which are characteristics of ions in an ionic compound with a large lattice enthalpy value?

A Large ionic radius and high ionic charge

B Small ionic radius and low ionic charge

C Large ionic radius and low ionic charge

D Small ionic radius and high ionic charge

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5 Which reaction has the largest positive value of $\Delta S^{\ominus}$?

A $CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$

B $2Al(s) + 3S(s) \rightarrow Al_2S_3(s)$

C $CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$

D $2S(s) + 3O_2(g) \rightarrow 2SO_3(g)$

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6 The standard enthalpy change of formation values of two oxides of phosphorus are:

$P_4(s) + 3O_2(g) \rightarrow P_4O_6(s) \quad \Delta H_f^{\ominus} = -1600 \text{ kJ mol}^{-1}$

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \quad \Delta H_f^{\ominus} = -3000 \text{ kJ mol}^{-1}$

What is the enthalpy change, in kJ mol^{-1}, for the reaction below?

$P_4O_6(s) + 2O_2(g) \rightarrow P_4O_{10}(s)$

A +4600

B +1400

C −1400

D −4600

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7 Which is a correct equation to represent the lattice enthalpy of magnesium sulfide?

A $MgS(s) \rightarrow Mg(s) + S(s)$

B $MgS(s) \rightarrow Mg(g) + S(g)$

C $MgS(s) \rightarrow Mg^{+}(g) + S^{-}(g)$

D $MgS(s) \rightarrow Mg^{2+}(g) + S^{2-}(g)$

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8 For the reaction:

$2CaO(s) \rightarrow 2Ca(s) + O_2(g)$

At 1 atmosphere the values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are both positive. Which statement is correct?

A $\Delta G^{\ominus}$ is temperature dependent.

B The change in entropy is the driving force of the reaction.

C At high temperatures ΔG is positive.

D The reverse reaction is endothermic.

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9 When $\Delta G^{\ominus}$ for a reaction is negative, the reaction is:

A fast.

B endothermic.

C reversible.

D spontaneous.

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10 In which of the following are the compounds CaF_2, $CaCl_2$, CsF and LiF arranged in **increasing** order of lattice enthalpy?

A $CaCl_2$, CaF_2, CsF, LiF

B CsF, LiF, $CaCl_2$, CaF_2

C $CaCl_2$, CaF_2, LiF, CsF

D LiF, CaF_2, CsF, $CaCl_2$

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 **a** **i** Define the term *standard enthalpy change of formation*.

(2 marks)

ii Write an equation, including state symbols, to show the formation of propane.

(1 mark)

b **i** Use standard enthalpies of formation (Appendix 3) to calculate the standard enthalpy change of combustion ($\Delta H_c^\ominus$) of propane, C_3H_8, for the following reaction.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

(5 marks)

ii Suggest, with a reason, whether the entropy change ($\Delta S^\ominus$) for the reaction would be positive or negative.

(2 marks)

iii Using standard entropy values in Appendix 3, calculate the entropy change for this reaction.

(2 marks)

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2 **a** Using the data below,

Compound	$C_4H_8(g)$	$CO_2(g)$	$H_2O(g)$	$O_2(g)$
$s^\ominus$ / J K^{-1} mol^{-1}	306	214	189	205

Calculate for the reaction, at 25°C,

$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g)$

$\Delta H^\ominus = -2545$ kJ mol^{-1}

i the standard entropy change, $\Delta S^\ominus$.

(2 marks)

ii the standard free energy change, $\Delta G^\ominus$.

(2 marks)

b Predict, giving a reason, the spontaneity of the reaction at both high and low temperatures.

(2 marks)

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Part C: Data-based question

Substance	**Standard enthalpy of formation, $\Delta H_f^\ominus$ / kJ mol^{-1}**	**Absolute entropy, $S^\ominus$ / kJ mol^{-1} K^{-1}**
C(s)	0.0	5.7
$CO_2(g)$	–393.5	213.6
$H_2(g)$	0.0	130.6
$H_2O(l)$	–285.9	69.9
$O_2(g)$	0.0	205.0
$C_3H_7COOH(l)$		226.3

The enthalpy change for the combustion of butanoic acid at 25°C is –2183.5 kJ mol^{-1}. The combustion reaction is:

$$C_3H_7COOH(l) + 5O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$$

a Write the balanced equation for the formation of butanoic acid from its elements.

(1 mark)

b Using the above data, calculate the standard enthalpy of formation, $\Delta H_f^\ominus$, for butanoic acid.

(3 marks)

c Calculate the standard entropy change, $\Delta S_f^\ominus$, for the formation of butanoic acid at 25°C.

(3 marks)

d Calculate the standard free energy of formation, $\Delta G_f^\ominus$, for butanoic acid at 25°C.

(2 marks)

e Is this reaction spontaneous at 25°C? Explain your answer.

(1 mark)

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Part D: Extended-response question

The following enthalpy changes (in kJ mol^{-1}) refer to sodium chloride and its constituent elements.

	Enthalpy / kJ mol^{-1}
$\Delta H^{\ominus}_{formation}$(sodium chloride)	–411
$\Delta H^{\ominus}_{atomization}$(sodium)	+109
$\Delta H^{\ominus}_{atomization}$(chlorine)	+121
1st ionization energy (sodium)	+494
1st electron affinity (chlorine)	–364

a **i** State the meaning of the + and – signs in the enthalpy values.

(1 mark)

ii Explain the meaning of the symbol $^{\ominus}$.

(1 mark)

b State an equation, including state symbols, for each of the above enthalpy changes.

(5 marks)

c The given values can be used to calculate the lattice enthalpy of sodium chloride.

i Define the term *lattice enthalpy*.

(1 mark)

ii Construct a Born–Haber cycle and hence calculate the lattice enthalpy of sodium chloride.

(4 marks)

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Total marks: 50

5 KINETICS

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 16: Kinetics.

By the end of this chapter, you should be able to:

- distinguish between the terms *rate constant*, *overall order of reaction* and *order of reaction*
- deduce the rate expression for a reaction, using experimental data
- solve problems involving the rate expression
- sketch, identify and analyse graphical representations for zero-, first-order and second-order reactions
- explain that reactions can occur in more than one step
- define *rate-determining step*
- describe the relationship between reaction mechanism, order of reaction and rate-determining step
- qualitatively describe the relationship between the rate constant (k) and temperature (T)
- determine activation energy (E_a) values from the Arrhenius equation using graphs.

IBO Assessment statements 16.1.1 to 16.3.2

Most areas of chemistry deal with *why* reactions occur and *what* the end result is. In contrast, **chemical kinetics** is concerned with reaction rates and *how* reactions proceed at a molecular level. Reaction rates are important in all areas of life; ideally, crops would grow quickly, cars would rust slowly and food would stay fresh for weeks. In no area is an understanding of chemical kinetics more important than in industry. To stay in business, companies must generate their products as quickly and cheaply as possible. Various factors—concentration, temperature, surface area, presence of catalysts—may be manipulated to optimise production. Rate studies and the application of stoichiometry to chemical kinetics allow reactions to be scrutinised in detail, thus enabling chemical engineers to develop more efficient industrial processes. This chapter will demonstrate how to analyse the rates of reacting systems using simple mathematics, and how to use the resultant data to describe the likely sequence of events occurring during a reaction.

Figure 5.0.1 Increased knowledge of chemical kinetics has resulted in faster, cleaner methods for producing important chemicals such as sulfuric acid.

5.1 RATE EXPRESSION

Interactive CW Animation
Rates of change

The **rate of reaction** is defined as 'the change in concentration of reactants or products with time', and therefore indicates how quickly reactants are converted into products. Refer to *Chemistry: For Use with the IB Diploma Programme Standard Level*, chapter 7, pages 217–218 for a reminder of how reaction rates are calculated. Recall that rates of reaction are expressed as positive values, most commonly with the units **mol dm^{-3} s^{-1}**.

Figure 5.1.1 shows how reaction rates may be calculated using the concentration–time graph for the general reaction.

$$R \rightarrow P$$

where R is the reactant and P is the product.

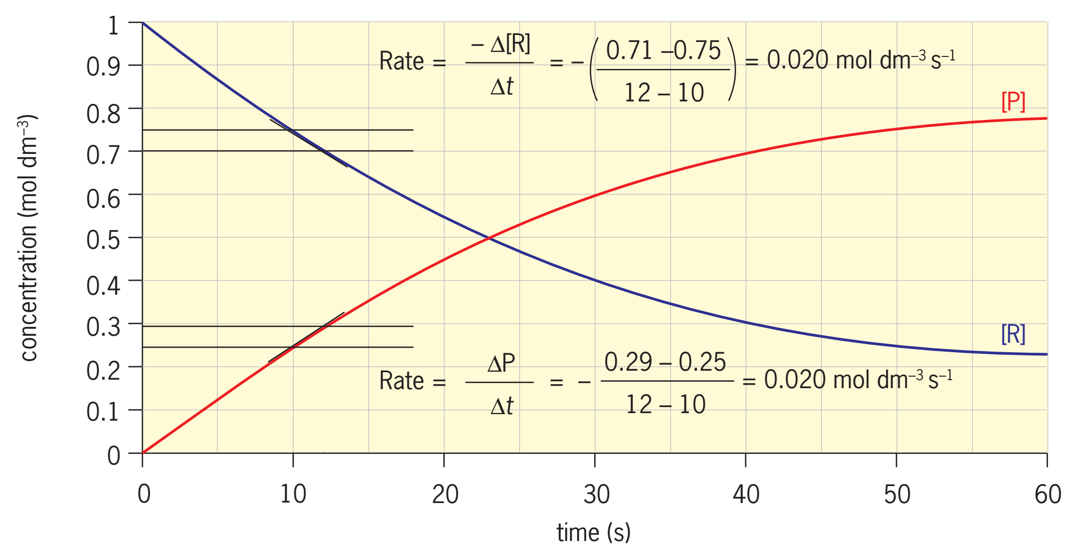

Figure 5.1.1 Change in concentrations of reactant and product with respect to time for the reaction R $\longrightarrow$ P. The reaction rate is fastest at the start of the reaction.

Note that the calculated reaction rates in figure 5.1.1 are identical for the two-second time period because the stoichiometric ratio of reactant to product is 1 : 1—the reactant, R, is consumed at the same rate as the product, P, is formed. Concentration–time graphs are a useful starting point for finding the relationship between the rate of reaction and the concentration of a particular reactant. This is illustrated in worked example 1.

Worked example 1

In acidic solution, hydrogen peroxide rapidly oxidizes iodide ions to molecular iodine:

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

An experiment was set up, and the iodine concentration was measured at various time intervals using colorimetric analysis. The initial concentration of hydrogen peroxide was 0.500 mol dm^{-3}. A large excess of iodide and hydrogen ions was used; their concentrations can be considered constant since they change negligibly during the course of this reaction. Find the relationship between reaction rate and hydrogen peroxide concentration.

Solution

The concentration of hydrogen peroxide remaining was deduced from the concentration of iodine present, using the fact that the stoichiometric reacting ratio is 1 : 1.

For example, if $[I_2] = 0.080$ mol dm^{-3}, $[H_2O_2] = 0.500 - 0.080 = 0.420$ mol dm^{-3}.

TABLE 5.1.1 RESULTS FOR THE OXIDATION OF IODIDE IONS BY HYDROGEN PEROXIDE

Time (s)	$[I_2]$ (mol dm^{-3}) product	$[H_2O_2]$ (mol dm^{-3}) reactant
0	0.000	0.500
10	0.080	0.420
20	0.148	0.352
30	0.204	0.296
40	0.252	0.248
60	0.325	0.175
100	0.413	0.087
150	0.464	0.036
200	0.485	0.015

The graph of hydrogen peroxide concentration versus time, figure 5.1.2, shows that the rate is at its maximum at the start of the reaction, and then slowly decreases.

The rate of reaction can be calculated using the graph of the values in table 5.1.1. In this instance,

$$\text{Rate} = -\frac{\Delta[H_2O_2]}{\Delta t}$$

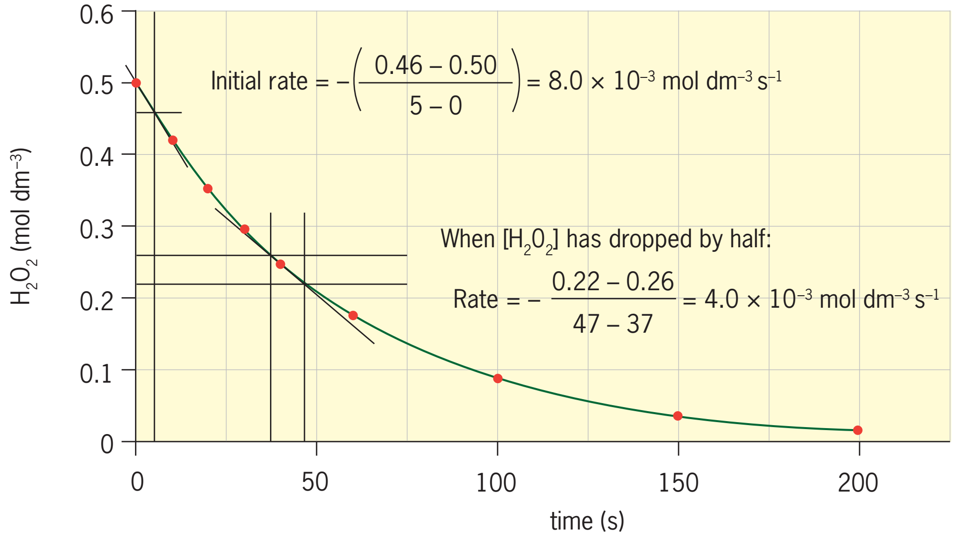

Figure 5.1.2 Change in the concentration of hydrogen peroxide with respect to time.

Using the graph to calculate the reaction rate at five different times gives the results shown in the table 5.1.2.

TABLE 5.1.2 RATE OF THE IODIDE–HYDROGEN PEROXIDE REACTION AT DIFFERENT TIMES

Time (s)	$[H_2O_2]$ (mol dm^{-3})	Rate of H_2O_2 consumption (mol dm^{-3} s^{-1})
0	0.500	8.0×10^{-3}
20	0.352	5.9×10^{-3}
40	0.250	4.0×10^{-3}
100	0.087	1.6×10^{-3}
200	0.015	3.0×10^{-4}

Graphing the reaction rate against the concentration of hydrogen peroxide yields a straight line (as shown in figure 5.1.3), implying that the reaction rate is directly proportional to the concentration of hydrogen peroxide:

$$\text{Rate} \propto [H_2O_2]$$

This means that the reaction rate decreases as the concentration of the hydrogen peroxide decreases.

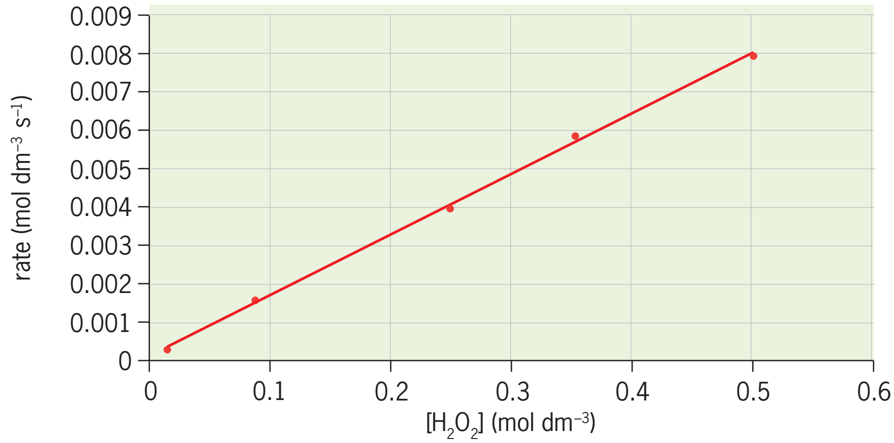

Figure 5.1.3 Reaction rate versus concentration of hydrogen peroxide.

Reaction order

For any reaction, with respect to a single reactant, R:

$$\text{Rate} \propto [R]^n$$

where n = order of reaction.

The **order of a reaction** indicates the relationship between the concentration of one or more reactants and the reaction rate. The common values of n are 0, 1 or 2. Respectively, these values of n correspond to **zero-**, **first-**, and **second-order reactions**.

AS **16.1.1**
Distinguish between the terms *rate constant, overall order of reaction,* and *order of reaction with respect to a particular reactant.*
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PRAC 5.1
Determination of the order of a reaction

In the iodide–hydrogen peroxide example given above, if $[H_2O_2]$ is doubled, the rate will double. Similarly, if $[H_2O_2]$ is halved, the rate will halve (as shown in figure 5.1.3). This reaction is said to be first order with respect to H_2O_2.

In this reaction, with respect to hydrogen peroxide:

$$\text{Rate} \propto [H_2O_2]^1$$

$n = 1$; this is why the reaction is termed first order.

Table 5.1.3 explains how the different orders of reaction will affect the reaction rate.

TABLE 5.1.3 ORDER OF REACTION WITH RESPECT TO A SINGLE REACTANT, R: A SUMMARY

Rate equation	Value of *n*	Order of reaction with respect to R	Explanation
Rate $\propto [R]^0$ but $[R]^0 = 1$ $\therefore$ Rate = a constant	0	Zero	The rate will not change if [R] is changed.
Rate $\propto [R]^1$	1	First	[R] and rate are directly proportional—the rate will change by the same factor as [R]. For example, tripling the concentration of R triples the rate.
Rate $\propto [R]^2$	2	Second	Since rate is directly proportional to $[R]^2$, doubling [R] would increase the rate fourfold; tripling it would increase the rate ninefold, etc.

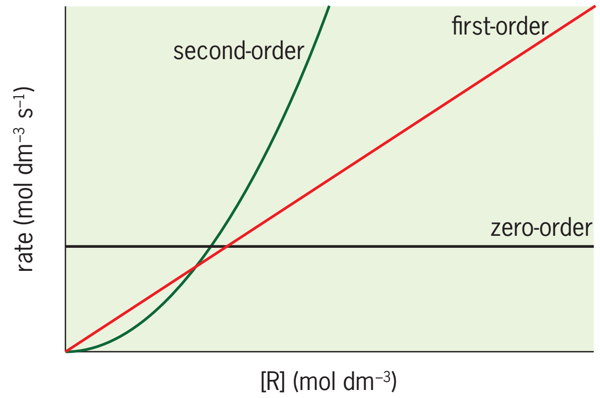


Figure 5.1.4 Zero-, first- and second-order reactions have different mathematical relationships between the concentration of a reactant, R, and the reaction rate.

The order of a reaction can only be determined from experimental data.

Note that when a reaction is first order with respect to one reactant it is not necessarily first order with respect to all or any other reactants.

Worked example 2

Consider the reaction:

$$A + B + 2C \rightarrow D + 2E$$

Let us imagine that an industrious student sets up four different reaction systems and measures the initial rate of reaction of each, obtaining the results listed in table 5.1.4. Determine the order of the reaction for each reactant.

TABLE 5.1.4 RESULTS OF THE A–B–C EXPERIMENTS

Experiment	Initial [A] (mol dm^{-3})	Initial [B] (mol dm^{-3})	Initial [C] (mol dm^{-3})	Initial rate of production of D (mol dm^{-3} s^{-1})
1	0.05000	0.05000	0.05000	3.125×10^{-6}
2	0.1000	0.05000	0.05000	6.250×10^{-6}
3	0.05000	0.1000	0.05000	1.250×10^{-5}
4	0.05000	0.05000	0.1000	3.125×10^{-6}

Solution

In experiment 2, the concentration of A is double that in experiment 1. The concentrations of B and C are unchanged.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{6.250 \times 10^{-6}}{3.125 \times 10^{-6}} = 2$$

Doubling the concentration of A doubled the rate. This implies that the rate is directly proportional to [A]:

$$\text{Rate} \propto [A]^1$$

This reaction is first order with respect to A.

In Experiment 3, the concentration of B is double that in experiment 1. The concentrations of A and C are unchanged.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{1.250 \times 10^{-5}}{3.125 \times 10^{-6}} = 4$$

Doubling the concentration of B quadrupled the rate. This implies that the rate is directly proportional to $[B]^2$:

$$\text{Rate} \propto [B]^2$$

This reaction is second order with respect to B.

In experiment 4, the concentration of C is double that in experiment 1. The concentrations of A and B are unchanged.

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.125 \times 10^{-6}}{3.125 \times 10^{-6}} = 1$$

Doubling the concentration of C had no effect on the rate. This implies that the rate is not proportional to [C].

$$\text{Rate} \propto [C]^0$$

This reaction is zero order with respect to C.

THEORY OF KNOWLEDGE

If logic is such an important source of reliable knowledge for scientists, how do chemists use logic to determine the order of a reaction? Using inductive reasoning, specific data is collected from experiments and combined into a relationship called a **rate expression** or **rate law**.

In worked example 2, a student set up four different reactions. Being sure to control all variables except for the initial concentration, the student changed the concentration of each reactant (A, B and C) in turn, and measured the initial rate of reaction (table 5.1.4). When sufficient reliable data had been collected, a series of inferences or general statements were made relating the concentration of each reactant to the initial rate of the reaction. For example, by comparing reations 1 and 2 it could be inferred that doubling the concentration of reactant A doubled the rate of the reaction (Rate $\propto [A]^1$). These inferences were then combined and expressed as a rate expression.

- Consider some of the possible uncertainties or limitations in relying on inductive reasoning to determine a rate expression.
- Since a rate expression can only be determined experimentally, is it still reliable knowledge? Explain.

Rate expression and rate constant

In worked example 2,

$$A + B + 2C \rightarrow D + 2E$$

it was found that

$$\text{Rate} \propto [A]^1$$

$$\text{Rate} \propto [B]^2$$

$$\text{Rate} \propto [C]^0$$

Combining these proportionality relationships gives the **rate expression** or **rate law** for this reaction:

$$\begin{aligned}\text{Rate} &= k[A][B]^2[C]^0\\ &= k[A][B]^2\end{aligned}$$

The rate expression mathematically describes the relationship between reaction rate and concentrations of reactants.

k is the **rate constant**; it is a constant value for a particular reaction as long as concentration is the only changing variable. Other changes, such as temperature or the presence of a catalyst, will change its value.

A very small *k* value tends to indicate a slow reaction rate, while a large *k* value indicates a fast reaction rate.

The general form of the rate expression is

$$\text{Rate} = k[R_1]^m[R_2]^n\ldots$$

where $R_1$and R_2 are reactants, and *m* and *n* are their respective, experimentally determined reaction orders.

PRAC 5.2
Determination of the overall order of a reaction

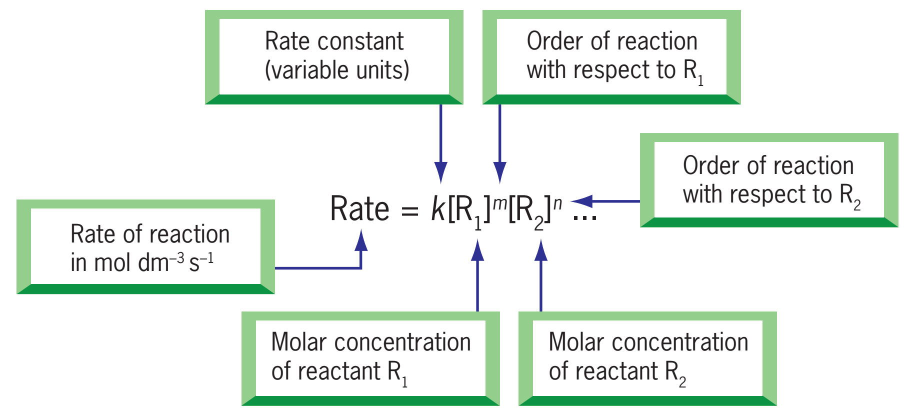


Figure 5.1.5 The rate expression.

The overall order of a reaction order is calculated by adding the orders of reaction with respect to each reactant.

For example, it has been experimentally determined that the reaction:

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

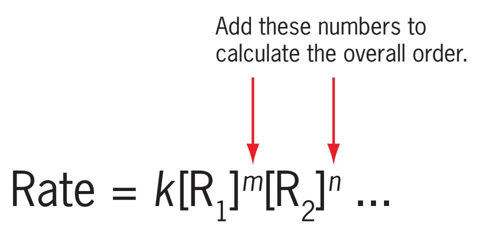
is first order with respect to the concentration of hydrogen, and second order with respect to the concentration of nitrogen(II) oxide. These relationships may be expressed as

$$\text{Rate} \propto [H_2] \qquad \text{and} \qquad \text{Rate} \propto [NO]^2$$

which, when combined, give the rate expression:

$$\begin{aligned}\text{Rate} &= k[H_2][NO]^2 \\ &= k[H_2]^1[NO]^2\end{aligned}$$

∴ The overall reaction order = 1 + 2 = 3 (third order).



Add these numbers to calculate the overall order.

$$\text{Rate} = k[R_1]^m[R_2]^n \ldots$$

Figure 5.1.6 The overall reaction order is the sum of the individual reaction orders with respect to each reactant.

Units of rate constants

Depending on the rate of reaction with respect to the various reactants, rate expressions may be made up of varying combinations of concentration terms. It is important that the units of the rate of reaction are always mol dm^{-3} s^{-1}, so to maintain this the units of the rate constant, *k*, will vary from reaction to reaction.

Worked example 3

Calculate the units of the rate constant for each of the following rate expressions.

a Rate = $k[A]$

b Rate = $k[A]^2$

Solution

a If Rate = $k[A]$

then $k = \dfrac{\text{Rate}}{[A]}$

The units of *k* are derived from this equation: $\dfrac{\cancel{\text{mol}}\ \cancel{\text{dm}^{-3}}\ \text{s}^{-1}}{\cancel{\text{mol}}\ \cancel{\text{dm}^{-3}}} = \text{s}^{-1}$

b If Rate = $k[A]^2$

then $k = \dfrac{\text{Rate}}{[A]^2}$

The units of *k* are derived from this equation:

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

The units of *k* change to allow the units of rate to be mol dm^{-3} s^{-1}.

The units of the rate constant will depend on the rate expression; the units of *k* must be such that the units of rate always work out as mol dm^{-3} s^{-1}.

Table 5.1.5 demonstrates that the overall order of reaction can be deduced from the units of *k*. For example, if the units of *k* are mol^{-2} dm^6 s^{-1}, the reaction must be third order overall.

TABLE 5.1.5 EXAMPLES OF GENERAL RATE EXPRESSIONS AND THE UNITS OF THE RATE CONSTANT, *k*

Rate expression	Overall order of reaction	Expression for *k*	Units of *k*
Rate = k	Zero order	k = Rate	mol dm^{-3} s^{-1}
Rate = $k[A]$	First order	$k = \frac{\text{Rate}}{[A]}$	s^{-1}
Rate = $k[A][B]$	Second order	$k = \frac{\text{Rate}}{[A][B]}$	mol^{-1} dm^{3} s^{-1}
Rate = $k[A]^2$	Second order	$k = \frac{\text{Rate}}{[A]^2}$	mol^{-1} dm^{3} s^{-1}
Rate = $k[A][B][C]$	Third order	$k = \frac{\text{Rate}}{[A][B][C]}$	mol^{-2} dm^{6} s^{-1}
Rate = $k[A]^2[B][C]$	Fourth order	$k = \frac{\text{Rate}}{[A]^2[B][C]}$	mol^{-3} dm^{9} s^{-1}

Deriving and using rate expressions

AS **16.1.2**
Deduce the rate expression for a reaction from experimental data.
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Determining the rate expression from experimental data involves measuring the initial reaction rate and initial reactant concentrations for a particular reaction system. Concentration must be the only changing variable (the independent variable). All other variables (such as temperature, pressure, volume, presence or absence of a catalyst, surface area of catalysts and solid reactants) should be kept constant throughout the series of experiments.

The general method to be followed is:

1. Set up the equipment, including rate-monitoring apparatus.
2. Conduct the first experiment, accurately recording initial reactant concentrations and initial rate.
3. Repeat the experiment, doubling or halving the initial concentration of one reactant only. (Other multiplication factors can be used, but a factor of 2 is most convenient.)
4. Repeat step 3 until enough information has been obtained to determine the reaction order with respect to each reactant.

Worked example 2 on page 133 illustrated how to use the method of initial rates to determine a rate expression. Worked example 4 shows how rate orders and rate constants may be determined experimentally.

Worked example 4

When nitrogen(II) oxide and oxygen are mixed in a vessel at high temperature, they react to form nitrogen(IV) oxide:

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

Five different experiments were conducted and closely monitored, yielding the results shown in table 5.1.6.

TABLE 5.1.6 RESULTS OF THE OXYGEN–NITROGEN(II) OXIDE EXPERIMENTS

Experiment	Initial [NO] (mol dm^{-3})	Initial [O_2] (mol dm^{-3})	Initial rate of production of NO_2 (mol dm^{-3} s^{-1})
1	0.100	0.100	1.50×10^{-5}
2	0.200	0.100	6.00×10^{-5}
3	0.100	0.200	3.00×10^{-5}
4	0.100	0.300	4.50×10^{-5}
5	0.300	0.100	1.35×10^{-4}

Use this data to find:

a the order of reaction with respect to NO

b the order of reaction with respect to O_2

c the rate expression

d the overall reaction order

e the value of the rate constant, *k*, with units.

Solution

a In experiment 2, the initial concentration of NO is double that of experiment 1. The initial concentration of O_2 is unchanged.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{6.00 \times 10^{-5}}{1.50 \times 10^{-5}} = 4$$

Doubling the concentration of NO quadrupled the rate. This implies that the rate is directly proportional to $[NO]^2$:

$$\text{Rate} \propto [NO]^2$$

This reaction is second order with respect to NO.

b In experiment 3, the initial concentration of O_2 is double that in experiment 1. The initial concentration of NO is unchanged.

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{3.00 \times 10^{-5}}{1.50 \times 10^{-5}} = 2$$

Doubling the concentration of O_2 doubled the rate. This implies that the rate is directly proportional to $[O_2]$:

$$\text{Rate} \propto [O_2]$$

This reaction is first order with respect to O_2.

c Combining:

$$\text{Rate} \propto [NO]^2 \text{ and Rate} \propto [O_2]$$

gives the rate expression

$$\text{Rate} = k[NO]^2[O_2]$$

d Since

$$\text{Rate} = k[NO]^2[O_2]^1$$

the overall reaction order = $2 + 1 = 3$ (i.e. third order)

e Any set of experimental data from table 5.1.6 can be used to find the value of k that corresponds to the set of conditions used in these experiments. Using the data from experiment 5:

$$k = \frac{\text{Rate}}{[\text{NO}]^2[\text{O}_2]} = \frac{1.35 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{(0.300\ \text{mol dm}^{-3})^2(0.100\ \text{mol dm}^{-3})}$$

$$\therefore k = 0.015\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

Having derived the rate expression, it can be used to determine an instantaneous reaction rate, or rearranged to calculate the value of another variable.

CHEM COMPLEMENT

The slowest reaction

Without enzymes—biological catalysts—humans would not survive. None of the reactions in our bodies would occur fast enough to keep us alive. Enzymes, such as alcohol dehydrogenase, which helps convert ethanol to ethanal in the liver, ensure our bodies can respond to changes quickly and efficiently. Enzyme reactions are generally first-order, and have large rate constants.

Enzymes are usually named to correspond with the molecule or group of molecules they act on: maltase breaks down the sugar maltose, lipases break down lipids (fats) and phosphatases break down phosphate esters. Phosphate esters are extremely important molecules that are involved in vital body processes, such as hormone and energy production. The catalysed reaction of simple phosphate esters with water occurs in milliseconds. It has been found that the uncatalysed reaction has a rate constant of approximately 2×10^{-20} s^{-1}, making it the slowest known reaction. If you had a sample of 10 g of a particular phosphate monoester, it would take more than a trillion years (1×10^{12} years) for half of the sample to react. That's a long wait—especially considering the fact that the universe is only about 15 billion years old! This should give you some idea of how incredibly effective the phosphatase enzymes are. Another biochemical reaction that would proceed slowly without enzymes is peptide hydrolysis, the reaction that breaks down protein chains.

With a rate constant of about 10^{-10} s^{-1}, it would take hundreds of years to digest a steak in the absence of enzymes.

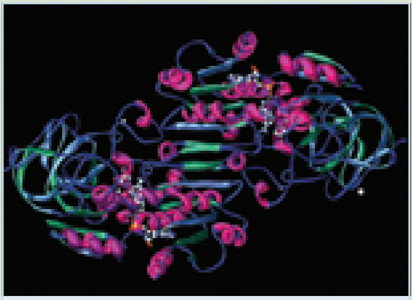


Figure 5.1.7 This enzyme, alcohol dehydrogenase, helps to break down alcohol in the body.

Determining an instantaneous reaction rate

AS **16.1.3**
Solve problems involving the rate expression. © IBO 2007

Given a set of data, values can be inserted into a previously derived rate expression and the reaction rate calculated. Care must be taken, as always, to ensure that all values are expressed in the correct units.

Worksheet 5.1
Rate expression problems

Worked example 5

The reaction

$$2\text{NO(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{NOCl(g)}$$

has the rate expression

$$\text{Rate} = k[\text{NO}]^2[\text{Cl}_2],\ \text{where}\ k = 1.3 \times 10^{-3}\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

Calculate the initial reaction rate when 0.400 mol of NO and 0.200 mol of Cl_2 are placed in a 2.0 dm^3 flask.

Solution

The molar concentrations of the reactants are calculated.

$$[NO] = \frac{0.400}{2.0} = 0.20 \text{ mol dm}^{-3}$$

$$[Cl_2] = \frac{0.200}{2.0} = 0.10 \text{ mol dm}^{-3}$$

$$\begin{aligned}\text{Rate} &= k[NO]^2[Cl_2] \\ &= 1.3 \times 10^{-3} \times 0.20 \times 0.10 \\ &= 2.6 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}\end{aligned}$$

The rate calculated by the rate expression is not normally defined in terms of the rate of consumption of a *particular* reactant or the rate of formation of a *particular* product. So the value of the rate obtained in calculations may appear somewhat ambiguous.

In worked example 5, the rate of 2.6×10^{-5} mol dm^{-3} s^{-1} means that (using the stoichiometric ratios in the balanced equation):

- the concentration of NO drops by 5.2×10^{-5} mol dm^{-3} every second
- the concentration of Cl_2 drops by 2.6×10^{-5} mol dm^{-3} every second
- the concentration of NOCl rises by 5.2×10^{-5} mol dm^{-3} every second.

CHEM COMPLEMENT

One complication in rate calculations is the fact that the presence of products interferes with the observed rate, since products may react to regenerate reactants in a back reaction.

Observed reaction rate = forward reaction rate − back reaction rate

For this reason, we generally only use initial reaction rates in calculations. Initially, the concentration of products is negligible and so no back reaction occurs. This means that the observed rate will be equal to the forward reaction rate only, and error is minimized.

Finding *k*

If enough information is given, it is possible to calculate the value of the rate constant *k*, as shown in worked example 4. Another example is given below.

Worked example 6

In a high temperature reaction, hydrogen bromide and oxygen combine to produce water and bromine:

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

The rate expression was determined by experiment to be

$$\text{Rate} = k[HBr][O_2]$$

In one experiment in which the concentrations of both reactants were 0.250 mol dm^{-3}, the rate was found to be 6.54×10^{-3} mol dm^{-3} s^{-1}.

Calculate the value of *k*, with the appropriate units.

Solution

$$\begin{aligned}k &= \frac{\text{Rate}}{[HBr][O_2]} = \frac{6.54 \times 10^{-3} \cancel{\text{mol}} \ \cancel{\text{dm}^{-3}} \text{ s}^{-1}}{0.250 \cancel{\text{mol}} \ \cancel{\text{dm}^{-3}} \times 0.250 \text{ mol dm}^{-3}} \\ &= 0.105 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\end{aligned}$$

Calculating the concentration of a reactant

In some instances, the only unknown is the concentration of a reactant. Rearranging the rate expression allows the unknown to be calculated.

Worked example 7

Hydrogen peroxide and iodide may follow several reaction paths in acidic solution, depending on the reaction conditions. One possible reaction produces the triiodide ion, I_3^-, and water:

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O(l)$$

For one set of reaction conditions, it was determined that

$$\text{Rate} = k[H_2O_2][I^-]$$

and

$$k = 1.2 \times 10^{-3}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

If initially there was 2.00 mol of iodide ions present in 4.00 dm^3 of solution, calculate the concentration of hydrogen peroxide that must have been present for the initial rate of reaction to be 2.34×10^{-4} mol dm^{-3} s^{-1}.

Solution

The initial concentration of iodide ions was:

$$[I^-] = \frac{2.00}{4.00} = 0.500\ \text{mol dm}^{-3}$$

$$[H_2O_2] = \frac{\text{Rate}}{k\left[I^-\right]} = \frac{2.34 \times 10^{-4}\ \text{mol dm}^{-3}\ \cancel{\text{s}^{-1}}}{1.2 \times 10^{-3}\ \cancel{\text{mol}^{-1}}\ \cancel{\text{dm}^{3}}\ \cancel{\text{s}^{-1}} \times 0.500\ \cancel{\text{mol}}\ \cancel{\text{dm}^{-3}}}$$

$$= 0.390\ \text{mol dm}^{-3}$$

Graphs showing reaction orders

AS 16.1.4
Sketch, identify and analyse graphical representations for zero-, first- and second-order reactions. © IBO 2007

If a reaction is zero order with respect to a particular reactant, changing the concentration of that reactant will have no effect on the reaction rate. For simplicity, consider the decomposition reaction

$$A \rightarrow B + C$$

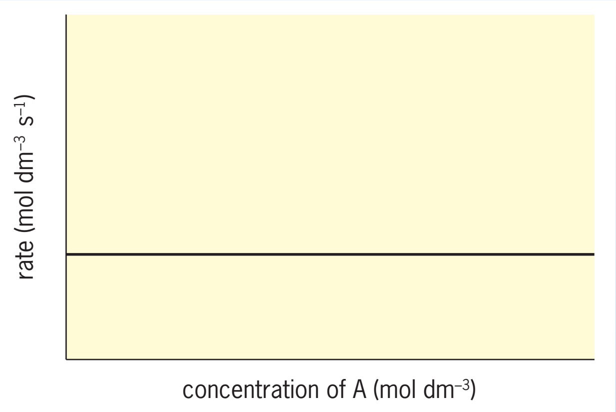


Figure 5.1.8 Rate–concentration graph for a reaction that is zero order with respect to reactant A.

If this reaction is zero order with respect to A:

$$\text{Rate} = k[A]^0 = k$$

Figure 5.1.8 shows the shape of the *rate–concentration* graph for such a reaction. The line has zero gradient because rate is constant.

As rate is constant, the concentration of A will drop by the same amount every second. The *concentration–time* graph is therefore a straight line with a negative gradient (figure 5.1.9).

The hydrogen peroxide–iodide reaction graphs at the beginning of this chapter (see worked example 1, p. 129) demonstrated the shapes of rate–concentration and concentration–time graphs for first-order reactions.

Consider the reaction

$$A \rightarrow B + C$$

which is first-order with respect to A. The rate expression would be:

$$\text{Rate} = k[A]$$

and hence

$$k = \frac{\text{Rate}}{[A]}$$

This means that graphing *rate* against *concentration* will produce a straight line with gradient equal to *k* (figure 5.1.10).

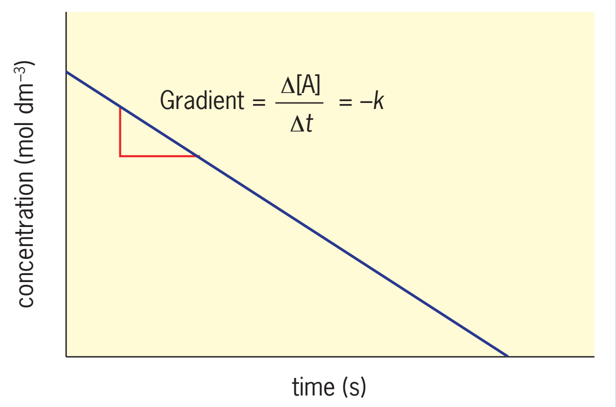


Figure 5.1.9 Concentration–time graph for a reaction that is zero order with respect to reactant A.

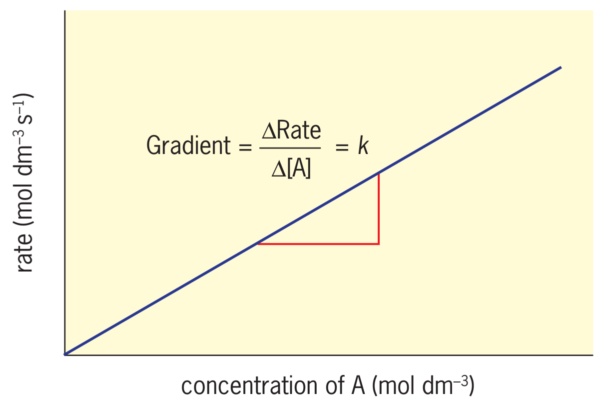


Figure 5.1.10 Rate–concentration graph for a reaction that is first order with respect to a reactant A.

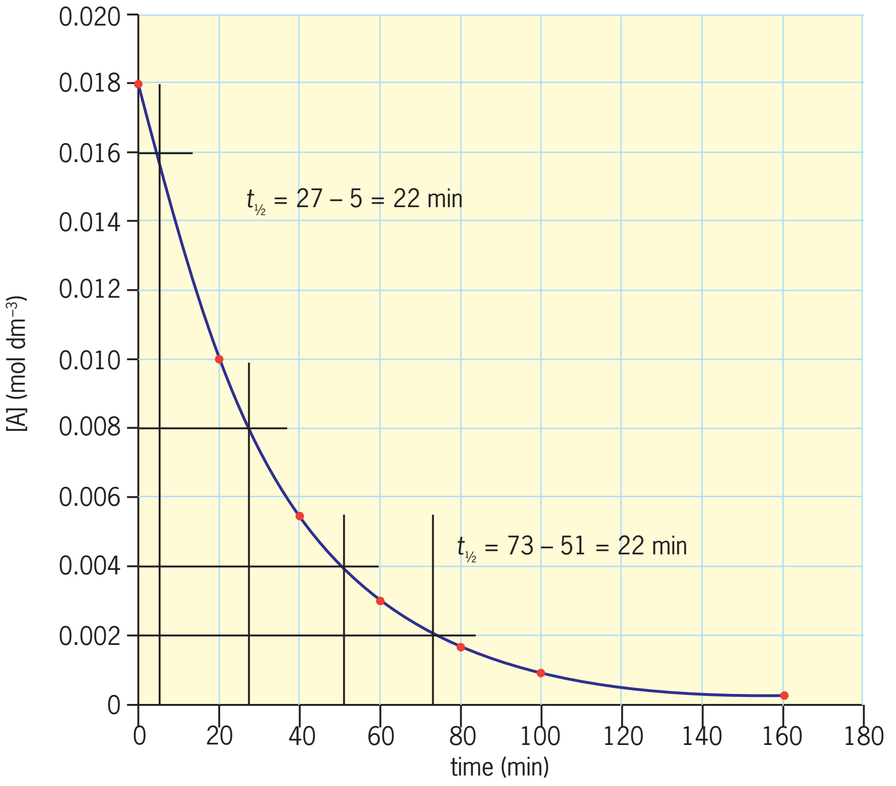


Figure 5.1.11 Concentration–time graph for a reaction that is first order with respect to reactant A.

First-order process

The *concentration–time* graph of a first-order reaction (figure 5.1.11) illustrates that the concentration of reactant A decreases in an exponential fashion. In fact, the concentration of A drops by half after a regular time interval, which is different for every reaction. The **half-life** ($t_{1/2}$) of the reaction is the time taken for the concentration of a reactant to drop to half of its original value.

If the reaction

$$A \rightarrow B + C$$

was second-order with respect to A, the rate expression would be:

$$\text{Rate} = k[A]^2$$

and hence:

$$k[A] = \frac{\text{Rate}}{[A]}$$

The *rate–concentration* graph for any second-order reaction will be a curve because the gradient changes as the concentration of the reactant changes, in contrast to the *rate–concentration* graphs for zero- and first-order reactions, which both have constant gradients.

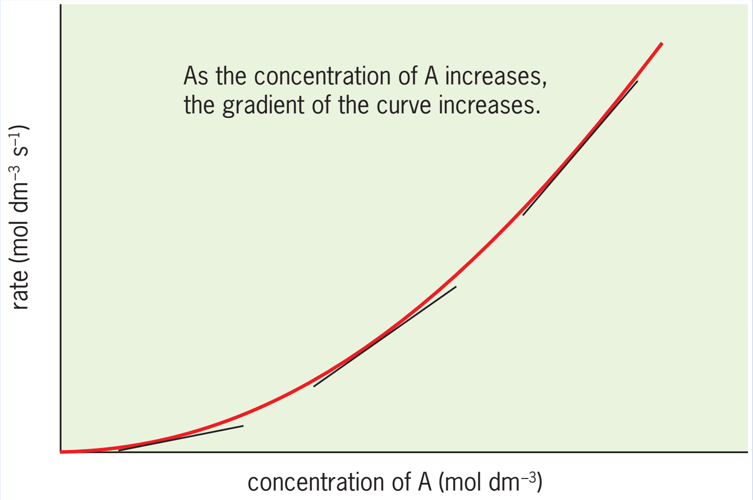


Figure 5.1.12 Rate–concentration graph for a reaction that is second order with respect to a reactant A.

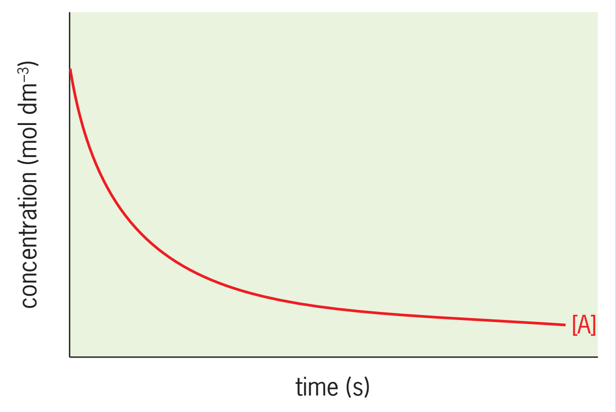


Figure 5.1.13 Concentration–time graph for a reaction that is second order with respect to reactant A.

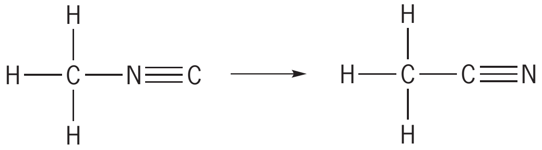
Like first-order reactions, the *concentration–time* graph of a second-order reaction (figure 5.1.13) is a curve; however, the rate (and hence the gradient of the curve) decreases much more quickly for a second-order reaction. Still, it can sometimes be hard to tell the two reaction orders apart just by looking at *concentration–time* graphs; *rate–concentration* graphs highlight the different reaction orders much more clearly.

Knowing the expected graph shapes for zero-, first- and second-order reactions provides a quick and easy way of determining reaction order. The graphs may also be analysed to determine quantities such as the instantaneous reaction rate, or k. The following example demonstrates how to use concentration–time graphs to find rate expressions and the value of k.

Worked example 8

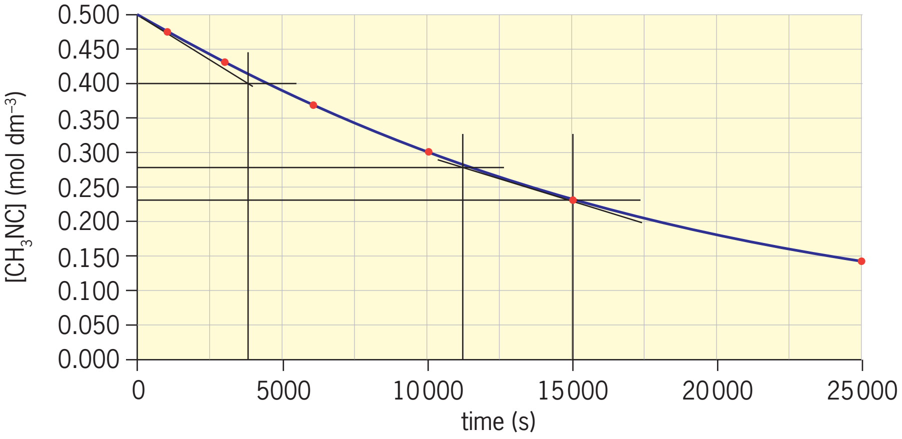
In an isomerization reaction at 200°C, methylisonitrile converts to ethanenitrile. Note that the group, –CN, inverts during this reaction.

Determine the order of this reaction.



Solution

The shape of the curve produced by graphing the concentration of methylisonitrile (CH_3NC) against time (figure 5.1.14) will indicate the order of this reaction. The suspected order can be confirmed by calculating two instantaneous reaction rates from the graph. The points at which the instantaneous rates are calculated are chosen carefully so that the second concentration of CH_3NC is double the first concentration of CH_3NC.



When $[CH_3NC] = 0.500$ mol dm^{-3}, rate $= -\left(\frac{0.400 - 0.500}{3750 - 0}\right) = 2.67 \times 10^{-5}$ mol dm^{-3} s^{-1}

When $[CH_3NC] = 0.250$ mol dm^{-3}, rate $= -\left(\frac{0.230 - 0.280}{15\,000 - 11\,200}\right) = 1.32 \times 10^{-5}$ mol dm^{-3} s^{-1}

Figure 5.1.14 Change in the concentration of methylisonitrile with time.

As shown on the graph:

when $[CH_3NC] = 0.250$ mol dm^{-3}, rate $= 1.32 \times 10^{-5}$ mol dm^{-3} s^{-1}

when $[CH_3NC] = 0.500$ mol dm^{-3}, rate $= 2.67 \times 10^{-5}$ mol dm^{-3} s^{-1}.

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{2.67 \times 10^{-5}}{1.32 \times 10^{-5}} = 2$$

Hence, the reaction is first-order with respect to methylisonitrile:

$$\text{Rate} = k[CH_3NC]$$

Section 5.1 Exercises

1 State the order of reaction with respect to a reactant, R, if:

a the rate of reaction doubles when [R] doubles

b the rate of reaction is unchanged when [R] triples

c the rate of reaction reduces by a factor of four when [R] is halved.

2 Calculate the average rate of production of carbon dioxide in mol dm^{-3} s^{-1} if 0.480 g of carbon dioxide is produced in a 2.00 dm^3 flask in 1.06 minutes, according to the reaction:

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

3 The rate expression for the reaction
$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$
is Rate $= k[Br^-][BrO_3^-][H^+]^2$

Assuming that all variables except concentration are kept constant, predict the effect on the rate of reaction if:

a $[Br^-]$ doubles (other reactant concentrations unchanged)

b $[BrO_3^-]$ halves (other reactant concentrations unchanged)

c $[H^+]$ triples (other reactant concentrations unchanged)

4 The reaction system $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$ was studied at 800°C, yielding the results listed in the table below.

Experiment	Initial [H_2] (mol dm^{-3})	Initial [NO] (mol dm^{-3})	Initial rate of reaction (mol dm^{-3} s^{-1})
1	0.0030	0.0030	2.25×10^{-3}
2	0.0030	0.0060	9.00×10^{-3}
3	0.0060	0.0030	4.50×10^{-3}

From these results, deduce:

a the order of reaction with respect to H_2

b the order of reaction with respect to NO

c the rate expression

d the overall reaction order

e the value of the rate constant, with units.

5 The decomposition of hydrogen iodide to its constituent elements at 700 K was studied using three separate experiments. The following results were obtained.

Experiment	Initial [HI] (mol dm^{-3})	Initial rate of reaction (mol dm^{-3} s^{-1})
1	0.0100	1.15×10^{-7}
2	0.0200	4.60×10^{-7}
3	0.0300	1.04×10^{-6}

From these results, deduce:

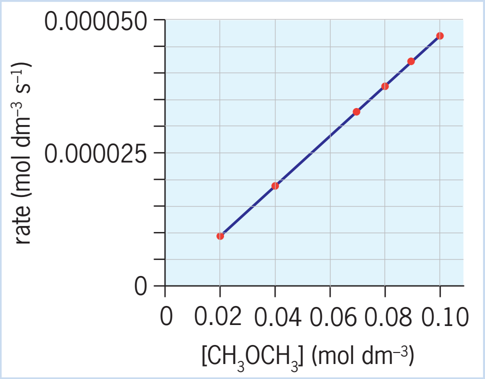
a the balanced reaction equation

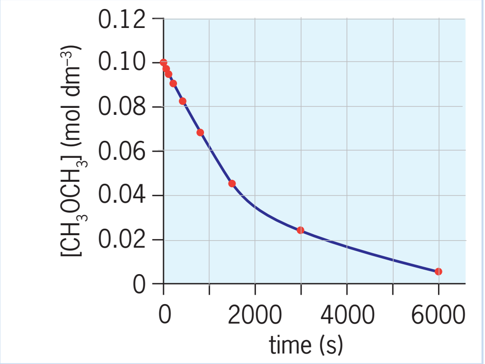
b the order of reaction with respect to HI

  c the rate expression
  d the overall reaction order
  e the value of the rate constant, with units.

6 The graphs opposite show the rate–concentration and concentration–time graphs for the decomposition of dimethyl ether at 500°C. Use these graphs to:
  a derive the rate expression
  b find the value of the rate constant at this temperature.

7 The reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ was found to be first order with respect to NO and second order with respect to O_2.
  a Deduce the rate expression.
  b The starting reactant concentrations are 1.0 mol dm^{-3}. On the one set of axes sketch the expected shape of the concentration–time graph for this reaction with respect to:
    i NO
    ii O_2
    iii NO_2





5.2 REACTION MECHANISM

Having looked at methods for determining the order of reactions, we can now turn to an examination of how reactions proceed at a molecular level. Consider the balanced equation for the combustion of ethane:

$$2C_2H_6(g) + 5O_2(g) \rightarrow 2CO_2(g) + 6H_2O(l)$$

According to this equation, two ethane molecules react with five oxygen molecules. Think about that for a moment. **Collision theory** explains that, for a reaction to occur, three things need to happen simultaneously:

1. Reactants must collide.
2. Reactants must collide in the correct orientation.
3. Reactants must collide with energy equal to or greater than the activation energy, E_a.

What is the probability that two ethane molecules and five oxygen molecules will simultaneously collide in the correct orientation with sufficient energy for reaction? It is far more likely that your hard-working Chemistry teacher will win the lottery, or be struck by lightning (several times!) than that a seven-molecule successful collision will ever occur.

The balanced reaction equation gives the overall picture, but it doesn't explain how the reaction occurs. It's a bit like a friend arriving at your house. You know where they started from, you know where they ended up; but you don't know the exact route they took to get there, or how fast they travelled on each part of the journey.

Very few reactions occur in one step; most are multi-step processes, in which each step rarely involves more than two molecules. Often, **intermediate** species are formed, which are a fundamental part of the process, but do not

Figure 5.2.1 The chance of being struck by lightning twice in an 80-year lifetime is 1 in 9 000 000. It is even less likely that more than three molecules will be involved in a simultaneous collision resulting in a reaction.

AS 16.2.1
Explain that reactions can occur by more than one step and that the slowest step determines the rate of reaction (rate-determining step). © IBO 2007

appear in the final reaction equation. The **reaction mechanism** is the actual step by step process by which a reaction occurs.

Reactions may proceed via many steps, or only one or two. The photochemical conversion of ozone to oxygen in the stratosphere

$$2O_3(g) \rightarrow 3O_2(g)$$

is believed to occur in two steps:

Step 1: $O_3(g) \rightarrow O_2(g) + O\cdot(g)$

Step 2: $O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$

Each step is called an **elementary step** or **elementary process**. In the first step, an ozone molecule decomposes to form diatomic oxygen and an oxygen atom (oxygen radical). In the second step, the reactive oxygen atom collides with another molecule of ozone, forming two diatomic oxygen molecules.

Adding the two elementary steps gives:

$$2O_3(g) + O\cdot(g) \rightarrow 3O_2(g) + O\cdot(g)$$

Cancelling species that are common to both sides gives the overall equation.

$$2O_3(g) + \cancel{O}\cdot(g) \rightarrow 3O_2(g) + \cancel{O}\cdot(g)$$

Overall: $2O_3(g) \rightarrow 3O_2(g)$

The equations for the elementary steps in a reaction mechanism must always add to give the balanced, overall equation for the reaction.

In this reaction, $O\cdot(g)$ is an intermediate—it is formed in one step and consumed in the next.

The **molecularity** of an elementary step describes how many molecules participate in that step. In the example above, step 1 is **unimolecular** and step 2 is **bimolecular**. If a step involved three molecules, it would be called **termolecular**. Termolecular reactions are very rare; it is 1000 times more likely that a bimolecular reaction will occur than a termolecular one.

Another way to describe the molecularity of a reaction is to give it a number:

- A unimolecular reaction has a molecularity of 1.
- A bimolecular reaction has a molecularity of 2.
- A termolecular reaction has a molecularity of 3.

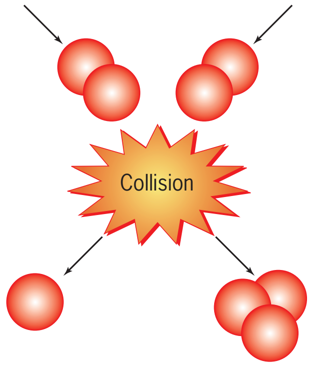
No examples of reactions with higher molecularity are known. This must be kept in mind when proposing possible reaction mechanisms. If you include a termolecular step, it makes your proposed mechanism unlikely; if you include a step in which more than three molecules simultaneously collide and react, it makes your proposed mechanism impossible and therefore incorrect.

Although rate expressions for overall reactions must be determined experimentally, rate expressions for elementary steps can be derived from the equation for that step. For step 2 of the ozone reaction:

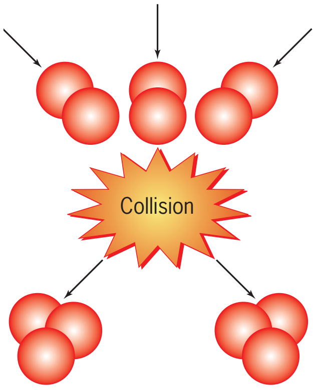
$$O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$$

two molecules must collide for a reaction to occur. Doubling the concentration of either reactant will double the likelihood of collision. This reaction must be first order with respect to both reactants and will have the rate expression

$$\text{Rate} = k[O_3][O\cdot]$$



bimolecular reaction



termolecular reaction

Figure 5.2.2 It is 1000 times more likely that a bimolecular reaction will occur than a termolecular one.

TABLE 5.2.1 RATE EXPRESSIONS FOR ELEMENTARY STEPS

General equation for elementary step	Example	Molecularity	General rate expression
$A \rightarrow B + C$	$O_3(g) \rightarrow O_2(g) + O\cdot(g)$	unimolecular	Rate = $k[A]$
$A + B \rightarrow C + D$	$O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$	bimolecular	Rate = $k[A][B]$
$2A \rightarrow B + C$	$2NO_2(g) \rightarrow NO_3(g) + NO(g)$	bimolecular	Rate = $k[A]^2$
$A + B + C \rightarrow D + E$	$ClO\cdot(g) + NO_2(g) + N_2(g) \rightarrow ClONO_2(g) + N_2^*(g)$	termolecular	Rate = $k[A][B][C]$
$2A + B \rightarrow C + D$	$2Cl\cdot(g) + CH_4(g) \rightarrow Cl_2(g) + CH_4^*(g)$	termolecular	Rate = $k[A]^2[B]$

The symbol * is used to indicate a high-energy state. Many termolecular reactions occur in the atmosphere and involve transitions from low-energy to high-energy states.

If the rate expression for an overall reaction is known, it can be used to test whether the process occurs in one step (rare) or in several steps (common).

A reaction such as

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

will obviously take place in more than one step because there is such a low probability of five molecules participating in a one-step reaction. Remember that no instances of one-step reactions involving more than three molecules have ever been found.

With a reaction such as

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

it is possible, though unlikely, that the reaction occurs in only one step. If it occurred in one step, the rate expression would be

$$\text{Rate} = k[NO_2]^2[F_2]$$

The experimentally determined rate expression for this reaction is

$$\text{Rate} = k[NO_2][F_2]$$

The rate expressions don't match, proving that the reaction must occur in two or more steps.

Figure 5.2.3 The rate-determining step in pizza production is the cooking of the pizza.

Rate-determining step

A certain take-away pizza shop has a production line involving four workers. The first person takes the pre-prepared base and covers it in tomato paste. The second person adds the toppings. The third person puts it in the oven, and takes it out again when cooked. The fourth person slices it up and puts it in the box. In this four-step process, the slowest step is the cooking of the pizza. This should take about 10 minutes, while the other steps should take a minute or less. The process can be summarized as:

Step 1: tomato paste on base	**Fast**
Step 2: toppings on pizza	**Fast**
Step 3: cooking	**Slow**
Step 4: slicing and boxing	**Fast**

The rate of pizza production depends almost entirely on step 3. The slowest step in a process is called the **rate-determining step**.

16.2.2
Describe the relationship between reaction mechanism, order of reaction and rate-etermining step.
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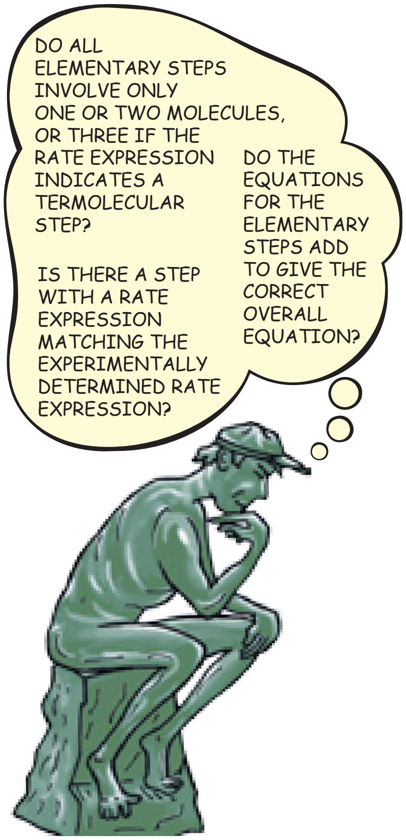


Figure 5.2.4 If the answer to all these questions is 'yes', your proposed reaction mechanism is valid.

Multi-step reactions can be considered in the same way; there is always one elementary step that has a slower rate than the others, and this step will govern the rate of the overall reaction. It doesn't matter if the slow step occurs at the beginning, middle or end of the reaction.

One example of a reaction in which the slow step occurs at the start of the reaction is the redox reaction between nitrogen(IV) oxide and carbon monoxide at 200°C:

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

If this reaction occurred in one step, the rate expression would be first order with respect to each reactant and second order overall:

$$\text{Rate} = k[NO_2][CO]$$

In fact, the rate expression has been experimentally determined as being second order with respect to nitrogen(IV) oxide and zero order with respect to carbon monoxide, and thus second order overall:

$$\text{Rate} = k[NO_2]^2$$

Since the rate is governed by the slowest step in the process, the proposed reaction mechanism must contain a slow step with a rate expression that matches the rate expression for the overall reaction.

Note that knowing the rate expression and the value of k provides evidence for a proposed reaction mechanism, but does not prove it.

So what is one plausible reaction mechanism for the nitrogen(IV) oxide–carbon monoxide reaction? From the rate expression, we know that one step must involve two nitrogen(IV) oxide molecules colliding. One possible mechanism is shown in table 5.2.2.

TABLE 5.2.2 PROPOSED MECHANISM FOR NITROGEN(IV) OXIDE–CARBON MONOXIDE REACTION

Step	Equation	Rate expression	Molecularity	Rate
1	$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$	Rate = $k[NO_2]^2$	Bimolecular	Slow
2	$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$	Rate = $k[NO_3][CO]$	Bimolecular	Fast

Three important points indicate the validity of this mechanism:

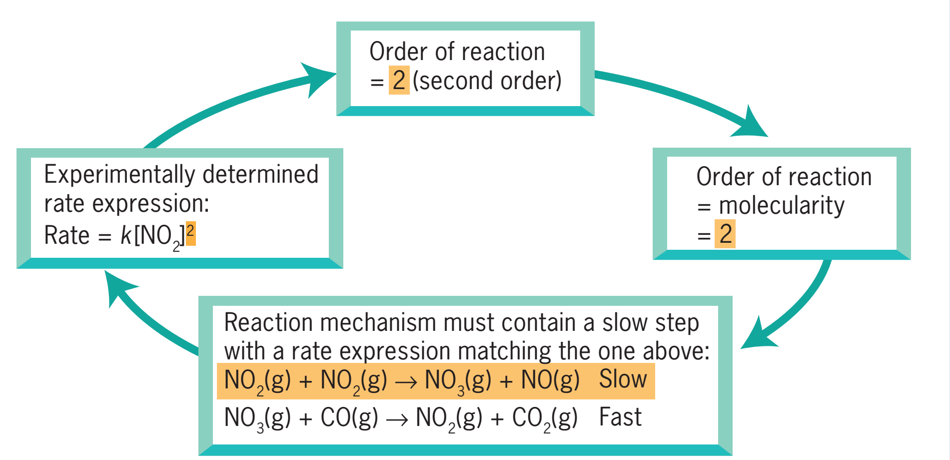
- Adding the two equations for the elementary steps gives the correct overall equation.
- It contains a slow step (the rate-determining step) with a rate expression matching the experimentally determined rate expression.
- No step involves more than two molecules colliding.

The time taken for the fast step contributes negligibly to the overall rate. This indicates that k for step 2 is much larger than k for step 1. The NO_3 intermediate is slowly produced in step 1, and then quickly consumed in step 2.

The importance of the rate-determining step is also reflected in the molecularity of the reaction.

The molecularity of the overall reaction is equal to the molecularity of the rate-determining step.

In this case, it is bimolecular (molecularity = 2), making the reaction second order overall.


Order of reaction = 2 (second order)

Order of reaction = molecularity = 2

Reaction mechanism must contain a slow step with a rate expression matching the one above:

$NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$ Slow

$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ Fast

Experimentally determined rate expression:

Rate = $k[NO_2]^2$

Figure 5.2.5 Kinetic relationships for the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$.

In this course, you will only be assessed on one-step or two-step mechanisms; however, it is useful to consider examples of reactions that occur in more than two steps. The reaction between hydrogen bromide and oxygen at 420°C has five molecules on the reactant side of the equation and so is likely to have a reaction mechanism involving more than two steps:

$$4HBr(g) + O_2(g) \rightarrow 2H_2O(g) + 2Br_2(g)$$

This is a second-order reaction, with the experimentally determined rate expression

$$\text{Rate} = k[HBr][O_2]$$

This means that any proposed mechanism must contain a slow step in which one HBr molecule and one O_2 molecule collide and react.

One proposed mechanism is shown in table 5.2.3.

TABLE 5.2.3 PROPOSED MECHANISM FOR THE HYDROGEN BROMIDE–OXYGEN REACTION

Step	Equation	Rate expression	Molecularity	Rate
1	$HBr(g) + O_2(g) \rightarrow HBrOO(g)$	Rate = $k[HBr][O_2]$	Bimolecular	Slow
2	$HBrOO(g) + HBr(g) \rightarrow 2HBrO(g)$	Rate = $k[HBrOO][HBr]$	Bimolecular	Fast
3	$HBrO(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$	Rate = $k[HBrO][HBr]$	Bimolecular	Fast
4	$HBrO(g) + HBr(g) \rightarrow H_2O(g) + Br_2(g)$	Rate = $k[HBrO][HBr]$	Bimolecular	Fast

In some cases, the rate expression may not be known, but the slow step may be determined via quantitative rate studies. Imagine that the reaction

$$2A + B + C \rightarrow 2D + E$$

occurs via the mechanism shown in table 5.2.4, and that rate studies had determined the initial rates shown, at constant reactant concentration.

TABLE 5.2.4 **MECHANISM AND RATES FOR THE A–B–C REACTION**

Step	Equation	Rate expression	Molecularity	Rate (mol dm^{-3} s^{-1})
1	$A + B \rightarrow D + F$	Rate = k[A][B]	Bimolecular	0.0810
2	$F + C \rightarrow E + A$	Rate = k[F][C]	Bimolecular	0.1000
3	$A + C \rightarrow D + G$	Rate = k[A][C]	Bimolecular	0.0001
4	$A + G \rightarrow C$	Rate = k[A][G]	Bimolecular	0.0990

Step 3 is much slower than the other three steps; thus, it is the rate-determining step, and the rate expression for the overall reaction is

$$\text{Rate} = k[\text{A}][\text{C}]$$

There are two molecules involved in the rate-determining step, therefore the reaction is bimolecular (molecularity = 2) and second order overall.

Although we have focused on multi-step reactions, many examples of one-step reactions exist, such as S_N2 reactions. One example is the dehalogenation of 2,3-dibromobutane using iodide ions:

$$CH_3CHBrCHBrCH_3 + I^- \rightarrow CH_3CH = CHCH_3 + IBr + Br^-$$

Worksheet 5.2
Reaction mechanisms

Since the overall equation represents the only elementary step, this reaction will be second order, bimolecular, and have the rate expression:

$$\text{Rate} = k[CH_3CHBrCHBrCH_3][I^-]$$

THEORY OF KNOWLEDGE

The difficulty with relying on a rate expression to describe the relationship between the concentration of the reactants and the rate of the reaction is that nearly all reactions have more than one step. To understand how a chemical reaction occurs, chemists use deductive reasoning and intuition to predict a number of different possible reaction steps that might be consistent with the overall rate expression. Further experiments can be carried out, if needed, to eliminate the least likely mechanisms. The final proposed mechanism, however, is not proof that the reaction takes place this way, but it does provide chemists with a reaction pathway that can be compared with the experimentally determined rate expression to see if there is a match. If there is agreement, the proposed mechanism is more probable. If there is no agreement, this provides evidence to disprove the mechanism. Although chemists can never be entirely certain of the exact steps in a reaction mechanism, this does not prevent them from continuing the search for the most probable mechanism. Instead it reinforces the fact that scientific knowledge can be simultaneously certain and tentative, helping chemists remain open to new ideas, new theories and new knowledge.

- Why are we more likely to believe a proposed reaction mechanism when it is in agreement with the rate expression?

Section 5.2 Exercises

1 Identify which of the following reactions is more likely to occur in a single step and explain why.

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

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

2 Define these terms:

a elementary step

b reaction mechanism

c molecularity

d rate-determining step

e intermediate compound

3 Consider the reaction

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

Rate $= k[H_2][NO]^2$

a State the molecularity of the reaction.

b Propose a two-step mechanism.

c Identify any intermediates in your proposed mechanism.

4 **a** Identify what is wrong with this proposed mechanism for the reaction:

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

given that

Rate $= k[NO]^2[O_2]$

Step	Equation	Rate
1	$NO(g) + O_2(g) \rightarrow NO_3(g)$	Fast
2	$NO_3(g) + NO(g) \rightarrow 2NO_2(g)$	Fast

b Propose a valid mechanism for this reaction.

5 If the slow step in a particular reaction is

$NO(g) + NO(g) \rightarrow N_2O_2(g)$

deduce the rate expression.

6 Describe the molecularity of the following elementary steps.

a $N_2O(g) + Cl(g) \rightarrow N_2(g) + ClO(g)$

b $Cl_2(g) \rightarrow 2Cl(g)$

c $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$

7 Decomposition of hydrogen peroxide in the presence of iodide ions may proceed as shown in the table.

Step	Equation	Rate
1	$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq)$	Slow
2	$H_2O_2(aq) + IO^-(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq)$	Fast

a Write the overall reaction equation.

b Deduce the rate expression.

c State the molecularity of this reaction.

d Identify any intermediates and catalysts in this reaction mechanism.

CHEM COMPLEMENT

The *Challenger* disaster

Some reactions of oxygen with other substances are explosive. Explosions fall into two main categories: thermal explosions and chain reaction explosions.

In thermal explosions, the heat released by the reaction increases the rate of reaction. If the heat is trapped, the rate of reaction increases extremely quickly and can result in an explosion. Thermal explosions are more likely to occur at high pressures.

In chain reaction explosions, the number of radical intermediates (reactive species with unpaired electrons) increases as the reaction proceeds. Even if there are radicals present, an explosion may not occur. If the pressure is very low, the radicals lose energy by colliding with the container walls before hitting other molecules, so no explosion occurs. In a high pressure environment, the radicals tend to collide with each other. Their unpaired electrons pair up and the reaction stops, so no explosion occurs. However, if the radicals collide with other molecules and generate more radicals, the chain reaction continues and results in an explosion. This is how hydrogen and oxygen react. An explosion will only occur at certain temperatures and pressures.

One possible reaction mechanism is shown below:

Initiation (creates the first radicals):

$H_2(g) + O_2(g) \rightarrow HO_2(g) + H{\bullet}(g)$

Branching (continues to create radicals):

$H{\bullet}(g) + O_2(g) \rightarrow OH{\bullet}(g) + O{\bullet}(g)$

$O{\bullet}(g) + H_2(g) \rightarrow OH{\bullet}(g) + H{\bullet}(g)$

$OH{\bullet}(g) + H_2(g) \rightarrow H_2O(g) + H{\bullet}(g)$

$HO_2(g) + H{\bullet}(g) \rightarrow 2OH{\bullet}(g)$

$HO_2(g) + H_2(g) \rightarrow H_2O(g) + OH{\bullet}(g)$

The rate of reaction increases dramatically as the number of radicals increases. They are finally consumed in a termination step such as:

$OH{\bullet}(g) + H{\bullet}(g) + M(g) \rightarrow H_2O(g) + M{\bullet}(g)$

where M is any other molecule—its purpose in the reaction is to absorb excess energy.

The overall reaction is:

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

This reaction was at the heart of the loss of one of NASA's spacecraft more than 20 years ago. The world watched in horror as the much-anticipated and highly publicized launch of the *Challenger* space shuttle on 28 January 1986 went terribly wrong. A leak in one of the rocket motors allowed the hydrogen and oxygen fuels to mix, resulting in an explosion 73 seconds after liftoff that tore the shuttle apart, killing all seven astronauts on board. One of the crew killed was 28-year-old high school teacher Sharon Christa McAuliffe, a New Hampshire resident who had been selected from more than 11 000 applicants to be on board as part of the Teacher in Space Project.

Figure 5.2.6 The *Challenger* disaster — the result of a hydrogen–oxygen explosion. A faulty o-ring allowed the hydrogen and oxygen to mix, resulting in a chain reaction explosion.

5.3 ACTIVATION ENERGY

In general, an increase in temperature will increase the rate of reaction—a 10°C rise in temperature will approximately double the reaction rate. Not only do collisions occur more frequently at higher temperatures, but also a greater proportion of collisions are successful, since more collisions have energy equal to or greater than the **activation energy**, E_a. The kinetic energy of the colliding molecules provides the energy needed to start the reaction. The exceptions to this rule are reactions involving biological catalysts (enzymes), which denature at high temperatures, causing all reaction to cease.

Recall that the activation energy, E_a, is the minimum amount of energy needed for reaction to occur. The energy is needed to weaken the bonds in the reactants and form the high-energy **activated complex**, or **transition state**. Multi-step reactions proceed via a number of transition states. In this case, the activation energy will correspond to the energy needed to form the activated complex in the rate-determining step, since this reaction will have the largest E_a.

A reaction with a small E_a will proceed quickly (fast step), while a reaction with a large E_a will proceed much more slowly (slow step).

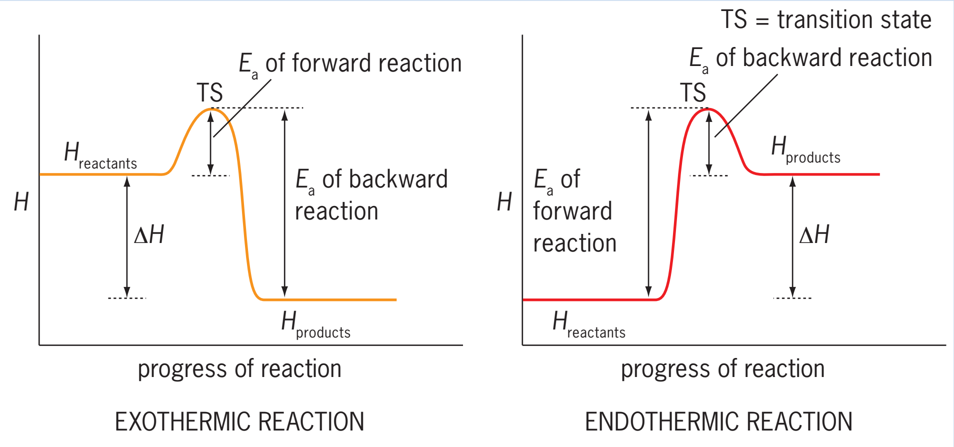


Figure 5.3.1 The activation energy, E_a, is the energy that is needed for a reaction to occur; it is the energy needed to break the bonds in the reactants and form the activated complex (transition state).

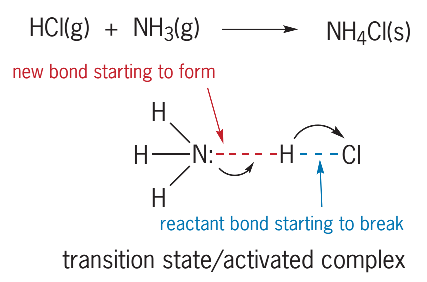


Figure 5.3.2 The transition state for the ammonia–hydrogen chloride reaction, in which, the acid, HCl, donates a proton to the base, NH_3, forming the ionic compound NH_4Cl.

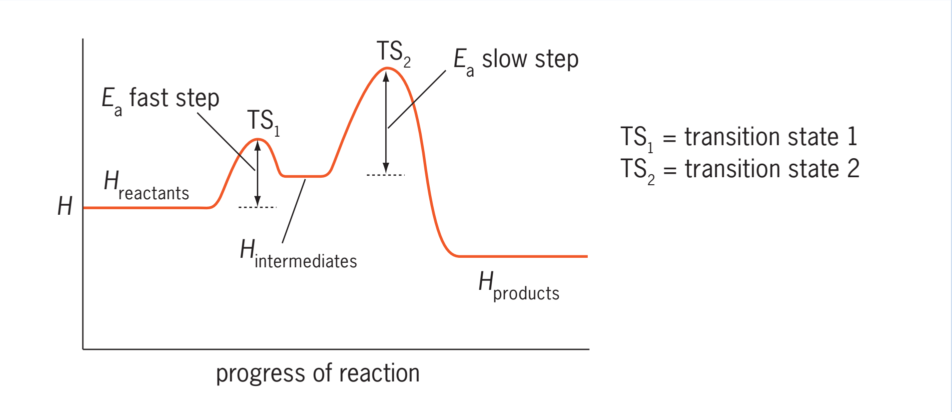


Figure 5.3.3 The slow step in a reaction mechanism will have the highest activation energy barrier.

The kinetic energy of moving particles is related to both their mass and velocity:

$$E = \frac{1}{2}mv^2$$

The absolute temperature (temperature in kelvin, K) will be proportional to the average kinetic energy of the particles:

$$\frac{1}{2}mv^2 \propto T$$

If the particles have constant mass, this can be simplified to

$$v^2 \propto T$$

This relationship between the velocities of particles in a sample and temperature is clearly illustrated by **Maxwell–Boltzmann distribution curve** (*Chemisty: For use with the IB Diploma Programme Standard Level,* p. 227).

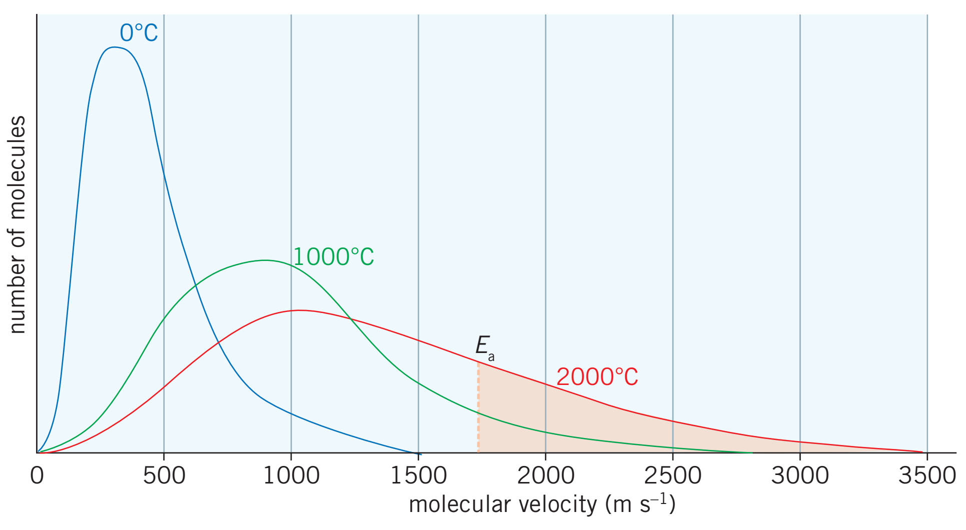


Figure 5.3.4 Maxwell–Boltzmann distribution curves showing the velocities of molecules in a gaseous reaction system at two different temperatures. Only molecules in the shaded section have enough energy to react.

The Arrhenius equation

It was Swedish chemist Svante Arrhenius in 1889 who first made use of the term *activation energy* to describe the minimum energy needed to induce a reaction.

From the Maxwell–Boltzmann curves (figure 5.3.4), it is clear that the rate of reaction will be proportional to the fraction of molecules (f) travelling with energy equal to or greater than E_a; that is, those in the shaded area of the graph. The relationship between the activation energy, the absolute temperature, and the fraction of molecules with energy equal to or greater than E_a is given by the equation:

$$\frac{\text{shaded area}}{\text{total area under curve}} = f = e^{-E_a/RT}$$

where R = the gas constant = 8.31 J K^{-1} mol^{-1}
T = temperature in kelvin (absolute temperature), and
e = 2.303 (base for natural logarithms).

Figure 5.3.5 Svante Arrhenius' theories were extremely important to the advancement of science.

At the start of this section, it was claimed that a 10°C (or 10 K) rise in temperature approximately doubles the rate. Let's see what effect that rise has on f in a reaction with $E_a = 237$ kJ mol^{-1}.

At 400 K:

$$f = e^{-(237\,000/8.31 \times 400)} = 1.08 \times 10^{-31}$$

Note that the units of E_a must be converted from kJ to J so that the units cancel. The units of the exponent are as follows. The units all cancel, so f is dimensionless.

$$\frac{\text{J mol}^{-1}}{\text{J K}^{-1}\ \text{mol}^{-1} \times \text{K}}$$

At 410 K:

$$f = e^{-237\,000/(8.31 \times 410)} = 6.17 \times 10^{-31}$$

$$\frac{f_{410}}{f_{400}} = \frac{6.17 \times 10^{-31}}{1.08 \times 10^{-31}} = 5.7$$

The 10 K rise in temperature increased the fraction of reactive molecules almost sixfold! Since the rate of reaction, and hence the rate constant k, is directly proportional to the fraction of molecules with energy equal to or in excess of E_a, it follows that:

$$k \propto e^{-E_a/RT}$$

Arrhenius realized that the rate of reaction and rate constant depend not only on the fraction of molecules with enough energy to react, but also on the fraction of collisions that occur in the correct orientation, and the number of collisions taking place every second. He incorporated all of these factors into the equation named after him—the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

where k = rate constant, and
A = Arrhenius constant or frequency factor.

The **Arrhenius constant, A,** is virtually constant for a particular reaction system over a wide temperature range, and is related to both the collision frequency and the probability that molecules are correctly orientated for reaction. The integrated form of the Arrhenius equation is also commonly used:

AS 16.3.1 Describe qualitatively the relationship between the rate constant (k) and temperature (T). © IBO 2007

$$\ln k = \ln A - \frac{E_a}{RT}$$

Certain sequential deductions can be made using the Arrhenius equation:

1 As the temperature increases, RT increases.

2 As RT increases, $\frac{E_a}{RT}$ decreases.

3 As $\frac{E_a}{RT}$ decreases, the quantity $-\frac{E_a}{RT}$ becomes less negative.

4 As $-\frac{E_a}{RT}$ becomes less negative, $e^{-E_a/RT}$ increases.

5 Since $k \propto e^{-E_a/RT}$, as $e^{-E_a/RT}$ increases, so does k.

The above can be summarized by the following sentence:

The magnitude of the rate constant will increase as the absolute temperature increases, and decrease as the absolute temperature decreases.

As previously described, this relationship is easily explained using collision theory.

Worked example 1 shows how the Arrhenius equation may be used.

Worked example 1

Nitrogen(V) oxide is a compound found in polar stratospheric clouds, where it contributes to ozone depletion. It undergoes a first-order, two-step decomposition with the overall equation:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

E_a for this reaction is 102 kJ mol^{-1}. At 318 K, $k = 4.82 \times 10^{-4}$ s^{-1}.

a Calculate the value of A at 318 K.

b Calculate the value of k at 373 K.

c Determine the absolute temperature when $k = 2.66 \times 10^{-4}$ s^{-1}.

Solution

a $k = Ae^{-E_a/RT}$

$$A = \frac{k}{e^{-E_a/RT}} = \frac{4.82 \times 10^{-4}}{e^{-102\,000/(8.31 \times 318)}} = 2.80 \times 10^{13}\ \text{s}^{-1}$$

b A is a constant, so the value of A calculated above can be used here.

$$k = Ae^{-E_a/RT} = 2.80 \times 10^{13}\ \text{s}^{-1} \times e^{-102\,000/(8.31 \times 373)} = 0.143\ \text{s}^{-1}$$

c This is most easily solved using the integrated form of the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Rearranging the above equation to solve for T gives

$$T = \frac{-E_a}{R \times (\ln k - \ln A)} = \frac{-102\,000}{8.31\left[\ln(2.66 \times 10^{-4}) - \ln(2.80 \times 10^{13})\right]} = 313\ \text{K}$$

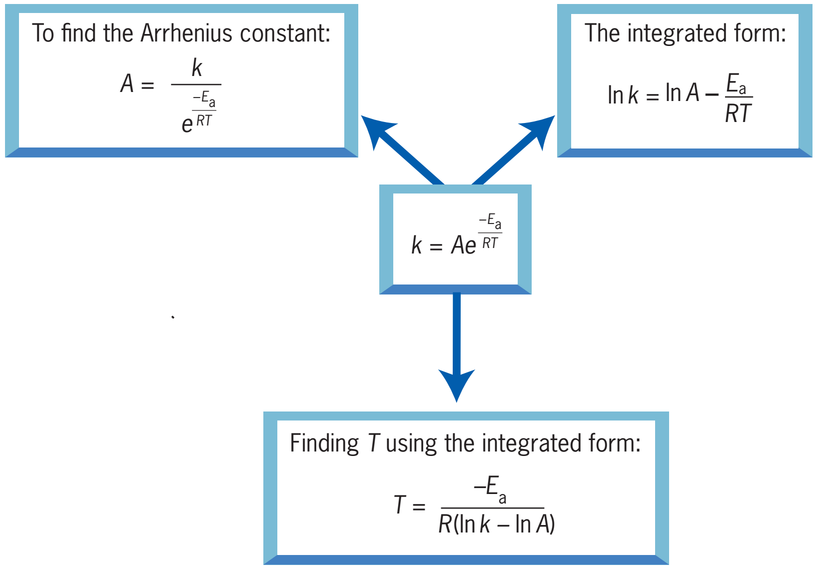


Figure 5.3.6 Useful forms of the Arrhenius equation.

Graphing the Arrhenius way

When

$$\ln k = \frac{-E_a}{RT} + \ln A$$

is written in the form

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \ln A$$

you might note that it corresponds to the equation of a straight line:

$$y = mx + c$$

In this case,

$$y = \ln k$$

$$m \text{ (the gradient)} = -\frac{E_a}{R}$$

$$x = \frac{1}{T}$$

$$c \text{ (the } y\text{-intercept)} = \ln A$$

This means that a graph of $\ln k$ (y-axis) against $\frac{1}{T}$ (x-axis) will yield a straight line that intercepts the y-axis at $\ln A$ and has a gradient equal to $\frac{-E_a}{R}$.

The following example demonstrates how to use such graphs to calculate the value of E_a for any reaction.

AS 16.3.2
Determine activation energy (E_a) values from the Arrhenius equation by a graphical method.
© IBO 2007

PRAC 5.3
Determining an activation energy

Worked example 2

Worked example 1 looked at the decomposition of nitrogen(V) oxide:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

It was stated that $E_a = 102$ kJ mol^{-1}.

We will use worked example 1 to see if we can arrive at the same E_a value using a graphical method.

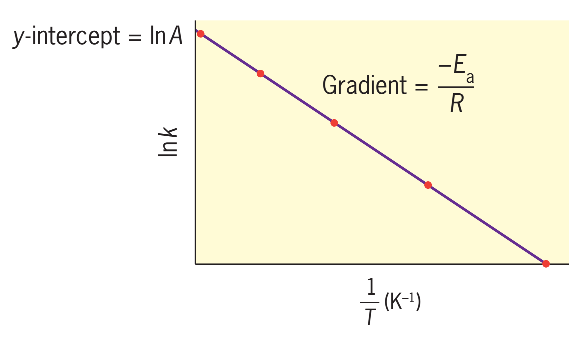


Figure 5.3.7 ln k versus $\frac{1}{T}$.

This system was analysed at five different temperatures, producing the rate constants given in table 5.3.1.

TABLE 5.3.1 RESULT OF NITROGEN(V) OXIDE EXPERIMENTS

Temperature (°C)	Temperature (K)	Rate constant (s^{-1})
10	283	4.08×10^{-6}
30	303	7.15×10^{-5}
50	323	8.78×10^{-4}
70	343	8.05×10^{-3}
90	363	5.78×10^{-2}

Solution

ln *k* and can be calculated from these values.

$\frac{1}{T}$ (K^{-1})	ln *k*
3.53×10^{-3}	−12.4
3.30×10^{-3}	−9.55
3.10×10^{-3}	−7.04
2.92×10^{-3}	−4.82
2.75×10^{-3}	−2.85

As expected, the graph of ln *k* versus $\frac{1}{T}$ is a straight line (figure 5.3.8).

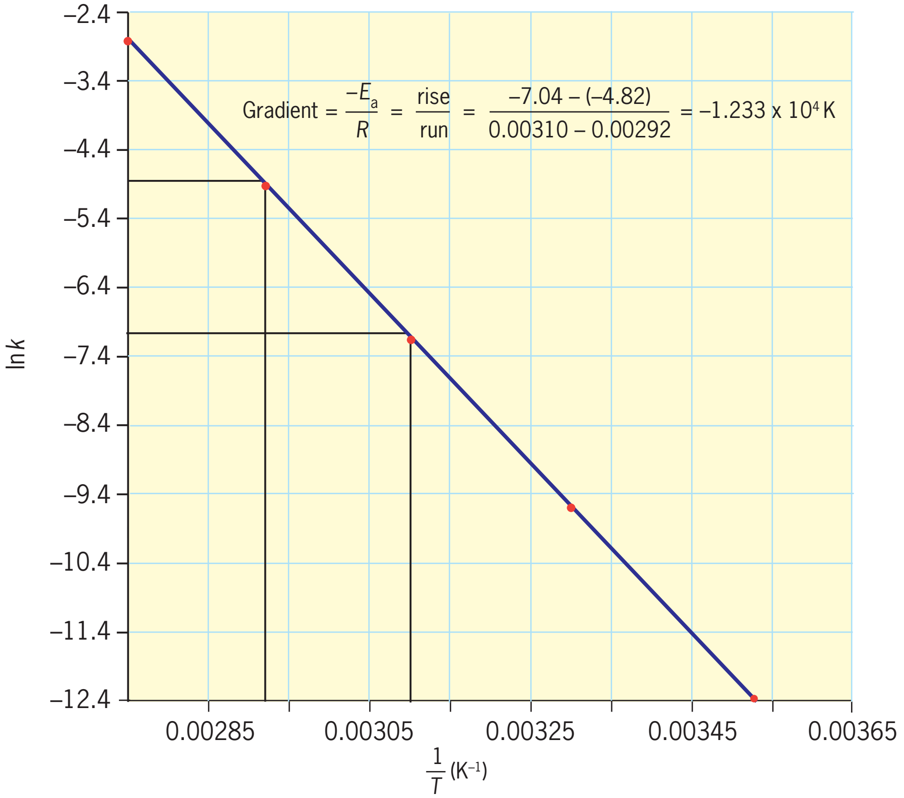


Figure 5.3.8 ln *k* versus $\frac{1}{T}$ for nitrogen(V) oxide decomposition.

Any two points from the above table may be used to calculate the gradient of the graph. The values could also be read from the graph itself, although with less accuracy.

Point 1: $\ln k = -4.82, \dfrac{1}{T} = 0.00292\ \text{K}^{-1}$

Point 2: $\ln k = -7.04, \dfrac{1}{T} = 0.00310\ \text{K}^{-1}$

$$\text{Gradient} = \frac{-7.04 - (-4.82)}{0.00310 - 0.00292} = -1.233 \times 10^4\ \text{K} = -\frac{E_a}{R}$$

$$\text{Hence, } E_a = R \times 1.233 \times 10^4 = 8.31\ \text{J}\ \cancel{\text{K}^{-1}}\ \text{mol}^{-1} \times 1.233 \times 10^4\ \cancel{\text{K}}$$

$$E_a = 102\,462\ \text{J mol}^{-1} = 102\ \text{kJ mol}^{-1}$$

This is the expected answer, so the method has been successful.

Note that $\ln k$ is dimensionless because logarithms don't have units.

Section 5.3 Exercises

1 In terms of collision theory, explain how a rise in temperature affects the rate of a chemical reaction.

2 Define the term *transition state*.

3 Calculate the fraction of molecules travelling with energy greater than 96 kJ in a sample at 280°C.

4 Dimethyl ether decomposes in a first-order reaction at 510°C:

$(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$

where $k = 6.8 \times 10^{-4}\ \text{s}^{-1}$ and $A = 3.458 \times 10^{-3}$.

a Calculate E_a in kJ mol^{-1}.

b Calculate the value of k at 550°C.

c Determine the absolute temperature when $k = 5.50 \times 10^{-4}\ \text{s}^{-1}$.

5 The temperature dependence of the rate constant of the reaction

$2A + 2B \rightarrow 3C$

is shown in the table below.

Temperature (°C)	Rate constant k (s^{-1})
25	1.35×10^{-7}
50	1.55×10^{-6}
75	1.25×10^{-5}

Use these values to calculate E_a for this reaction.

6 Describe the relationship between the rate constant, k, and absolute temperature.

7 For the reaction

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

$E_a = 165\ \text{kJ mol}^{-1}$

$A = 1.325 \times 10^{11}$

a Calculate the value of k when $T = 400$ K.

b Determine the temperature when $k = 3.45 \times 10^{-3}\ \text{s}^{-1}$.

Chapter 5 Summary

Terms and definitions

Activated complex (Transition state) The high-energy state where bonds in the reactants have started to break and bonds in the products have started to form.

Activation energy (E_a) The minimum amount of energy required to initiate a reaction.

Arrhenius constant (frequency factor, A) A constant related to both collision frequency and the probability that molecules are correctly orientated for reaction.

Arrhenius equation $k = Ae^{-E_a/RT}$

Bimolecular The molecularity of an elementary process in which two molecules collide and react.

Chemical kinetics The area of chemistry dealing with reaction rates and how reactions proceed on a molecular level.

Collision theory A theory that explains rates of reaction on a molecular level.

Elementary step (elementary process) A step in a reaction mechanism.

First-order reaction A reaction conforming to the rate expression Rate = $k[A]$.

Half-life The time taken for the concentration of a reactant to decrease by half.

Intermediate A species that features in a reaction mechanism, but not in the overall equation.

Maxwell–Boltzmann distribution curve A graph showing the distribution of particle velocities in a gas at a certain temperature.

Mol dm^{-3} s^{-1} The usual units of rate; equivalent to M s^{-1} or mol L^{-1} s^{-1}.

Molecularity The number of molecules involved in an elementary step; the molecularity of the overall reaction is equal to the molecularity of the rate-determining step.

Order of a reaction Indicates the relationship between the concentration of one or more reactants and the reaction rate.

Rate constant (k) Proportionality constant that features in both the rate expression and the Arrhenius equation.

Rate-determining step The slowest step in a reaction mechanism.

Rate expression (rate law) An expression of proportionality between concentration of reactants and rate, having the general form Rate = $k[R_1]^m[R_2]^n\ldots$

Rate of reaction The change in the concentration of a reactant or product with respect to time.

Reaction mechanism The step by step process by which a reaction occurs.

Second-order reaction A reaction conforming to the rate expression Rate = $k[A]^2$ or Rate = $k[A][B]$.

Termolecular The molecularity of an elementary process in which three molecules collide and react.

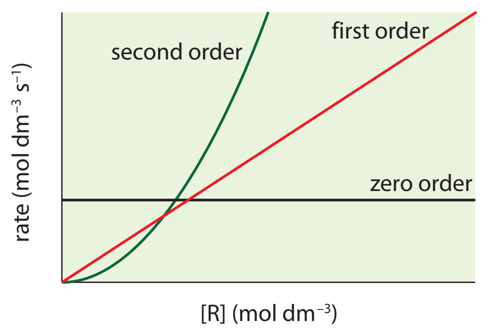
Transition state *see* Activated complex.

Unimolecular The molecularity of an elementary process in which one molecule reacts and collision with another molecule is not necessary.

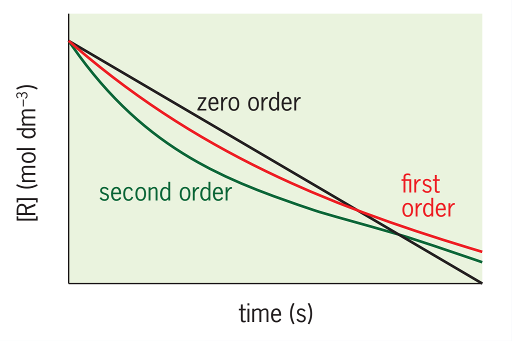
Zero-order reaction A reaction conforming to the rate expression Rate = k.

Concepts

- Rate of reaction $= -\dfrac{\Delta R}{\Delta t} = \dfrac{\Delta P}{\Delta t}$
- If a reaction is zero order with respect to a particular reactant, changing the concentration of the reactant will not change the rate.
- If a reaction is first order with respect to a particular reactant, the rate will be directly proportional to the reactant's concentration.
- If a reaction is second order with respect to a particular reactant, the rate will be directly proportional to the square of the reactant's concentration.



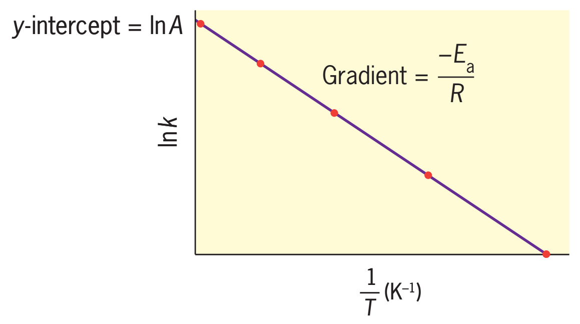
Rate–concentration graphs for zero-, first- and second-order reactions.



Concentration–time graphs for zero-, first- and second-order reactions.

- The general form of the rate expression is Rate = $k[R_1]^m[R_2]^n$…
- Adding the exponents m, n etc in the above expression will yield the overall order of reaction.
- k is the rate constant, a proportionality constant in the rate expression.
- The rate expression can be deduced using the method of initial rates.
- No reaction of higher molecularity than termolecular is known.
- The reaction mechanism shows the step-by-step reaction process.
- The slowest step in a reaction mechanism is the rate-determining step.
- A reaction mechanism must contain an elementary step which has a rate expression matching the experimentally determined rate expression.
- The overall molecularity of a reaction is equal to the molecularity of the rate-determining step.
- The activation energy of a reaction is the minimum energy that colliding molecules must possess in order to react; it is the energy needed to form the activated complex (transition state).
- Each elementary step will have its own activation energy and transition state.
- The activation energy of the overall reaction is equal to the activation energy of the rate-determining step.
- The Arrhenius equation shows how k and temperature are related (as one increases, so does the other): $k = Ae^{-E_a/RT}$
- The integrated form of this equation is

  $\ln k = -\dfrac{E_a}{RT} + \ln A$.
- A graph of $\ln k$ against $\dfrac{1}{T}$ will allow E_a to be calculated.



Graph of ln k versus $\dfrac{1}{T}$.

Chapter 5 Review questions

1 For the reaction

$2A + 2B \rightarrow C + D$

the following data was obtained.

[A] (mol dm^{-3})	[B] (mol dm^{-3})	Relative initial rate
0.0100	0.0100	1
0.0200	0.0100	2
0.0100	0.0200	4

a Deduce the order of reaction with respect to each reactant, and hence find the rate expression.

b Explain why it is unlikely that this reaction occurs in only one step.

c Propose a mechanism for this reaction.

d State the molecularity of this reaction.

2 For the reaction system

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

Rate = $k[A]^2$, $k = 1.23 \times 10^{-2}$ at 800 K

state whether the following statements are true or false.

a The units of k are s^{-1}.

b The rate will not change when [B] is doubled.

c k will have a different value at 200 K.

d The overall reaction order is third order.

3 The reaction

$2A + B + C \rightarrow D + 2E$

has the rate expression

Rate = $k[B]^2[C]$

a State the overall order of this reaction.

b Calculate the value of k, with units, if rate = 4.39×10^{-1} mol dm^{-3} s^{-1} and the concentration of all three reactants is 0.0500 mol dm^{-3}.

4 Explain which of these reactions will have the faster rate.

Reaction A: $E_a = 65$ kJ mol^{-1}, $\Delta H = -25$ kJ mol^{-1}

Reaction B: $E_a = 85$ kJ mol^{-1}, $\Delta H = -25$ kJ mol^{-1}

5 Explain what the A stands for in the Arrhenius equation.

6 Dimethylhydrazine and iodine react as follows:

$$(C_2H_5)_2(NH)_2(aq) + I_2(aq) \rightarrow 2HI(aq) + (C_2H_5)_2N_2(aq)$$

The rate of reaction is followed using colorimetric analysis.

In one set of reactions, the results shown in the table below were obtained.

$[(C_2H_5)_2(NH)_2]$ (mol dm^{-3})	$[I_2]$ (mol dm^{-3})	Initial reaction rate (mol dm^{-3} s^{-1})
0.150	0.100	1.55×10^{-6}
0.150	0.150	2.33×10^{-6}
0.300	0.100	3.10×10^{-6}
0.400	0.400	1.65×10^{-5}

a Deduce the order of reaction with respect to each reactant, and hence find the rate expression.

b Calculate k.

c Propose a mechanism for this reaction.

d Given the mechanism you proposed in part **c**, deduce the molecularity of this reaction.

7 Consider the reaction

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

with the rate expression Rate = $k[NO]^2[O_2]$.

a Describe how the initial rate of reaction compares with the rate when the NO concentration has decreased by half.

b State the molecularity of this reaction

c Explain whether this could be a one-step process.

d Describe the effect that heating the system would have on the value of k.

8 **a** Calculate the fraction of molecules having energy in excess of 120 kJ in a gas sample at 300°C.

b Describe how the fraction changes when the temperature is increased by 20°C.

9 **a** Propose two different mechanisms for the reaction

$A + 2B + C \rightarrow D + 2E$

given that Rate = $k[A][B]$.

b State the molecularity of this reaction.

10 Consider the following reaction:

$H_2(g) + 2ICl(g) \rightarrow 2HCl(g) + I_2(g)$

Rate = $k[H_2][ICl]$

a State the molecularity of the reaction.

b Propose a two-step mechanism.

c Identify any intermediates in your proposed mechanism.

11 Explain whether an elementary step can ever be identical to the overall reaction equation.

12 Explain whether the Arrhenius equation can be applied to reactions of any order, or only to first-order reactions.

13 The reaction

$A + B + C \rightarrow D + E$

was found to be zero order with respect to A and second order with respect to B.

a Sketch the shape of the rate–concentration graph with respect to A.

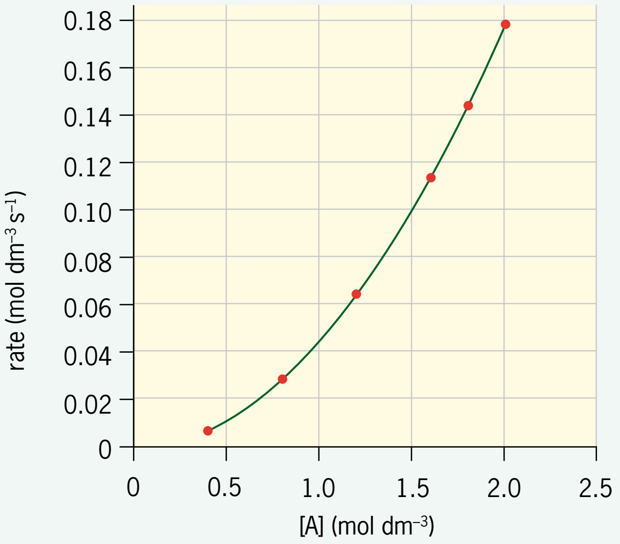
b Sketch the shape of the concentration–time graph with respect to B.

c Derive the rate expression for this reaction.

d Propose a mechanism for this reaction, identifying the rate-determining step.

14 Explain why the units of k are different for each reaction order.

15 The following rate–concentration graph is for the reaction $2A \rightarrow C + D$.



From the graph, deduce the order of this reaction and hence write the rate expression. Show all working and reasoning.

16 The reaction of 2-methyl-2-chloropropane with hydroxide ions forming 2-methyl-2-propanol (isobutanol) and chloride ions is a two-step process:

Step 1: $CH_3C(CH_3)_2Cl \rightarrow CH_3C^+(CH_3)_2 + Cl^-$
Rate $= k_1[CH_3C(CH_3)_2Cl]$

Step 2: $CH_3C^+(CH_3)_2 + OH^- \rightarrow CH_3C(CH_3)_2OH$
Rate $= k_2[CH_3C^+(CH_3)_2][OH^-]$
$k_2 > k_1$

a Identify the rate-determining step.

b State the molecularity of step 1.

17 Identify two factors that will change the value of k for a particular reaction.

18 A first-order elementary reaction of the type $A \rightarrow$ products has $k = 5.43 \times 10^{-4}\ s^{-1}$ at 250°C and $E_a = 27\ kJ\ mol^{-1}$.

a Calculate the value of the Arrhenius constant.

b Calculate the value of k when $T = 800$ K.

c Determine the absolute temperature when $k = 2.13 \times 10^{-6}\ s^{-1}$.

19 For a graph of $\ln k$ versus $\frac{1}{T}$, find the value of the gradient.

20 The temperature dependence of the rate constant of the reaction

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

is shown in the table below.

Temperature (°C)	Rate constant k (mol^{-1} dm^3 s^{-1})
327	2.8×10^{-2}
427	1.3
527	23

Use these values to calculate the values of E_a and the Arrhenius constant for this reaction.

Web Destinations www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter.

Part A: Multiple-choice questions

1 The following experimental data was obtained for the reaction X + Y → products.

[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
0.10	0.10	4.0×10^{-4}
0.20	0.20	1.6×10^{-3}
0.50	0.10	1.0×10^{-2}
0.50	0.50	1.0×10^{-2}

What is the order of reaction with respect to X and the order of reaction with respect to Y?

A 2 and 0

B 0 and 2

C 2 and 1

D 1 and 0

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2 Use the information below to deduce the rate equation for the hypothetical reaction:

X + Y → Z

[X] / mol dm^{-3}	[Y] / mol dm^{-3}	Relative rate
0.01	0.01	1
0.02	0.01	4
0.02	0.02	4

A Rate = k[X][Y]

B Rate = $k[X]^2$

C Rate = $k[Y]^2$

D Rate = $k[X]^2[Y]^2$

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3 The reaction between NO_2 and CO to give NO and CO_2 is thought to occur by the following mechanism:

$NO_2 + NO_2 \rightarrow NO + NO_2$ slow

$NO_3 + CO \rightarrow NO_2 + CO_2$ fast

What is the rate equation?

A Rate = $k[NO_2][CO]$

B Rate = $k[NO_3][CO]$

C Rate = $k[NO_2]^2[CO]$

D Rate = $k[NO_2]^2$

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4 The rate equation for the reaction between O_2 and NO is

Rate = $k[O_2][NO]^2$

By what factor would the rate of this reaction increase if the concentrations of O_2 and NO are both doubled?

A $\frac{1}{8}$

B 3

C 4

D 8

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5 The rate constant for a certain reaction has the unit **concentration time^{-1}**. What is the order of reaction?

A 0

B 1

C 2

D 3

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6 Which of the following statements regarding activation energy is(are) correct?

I In an endothermic reaction the activation energy for the reverse reaction is smaller than that for the forward reaction.

II Increasing temperature increases the rate of a chemical reaction by lowering the activation energy.

A I only

B II only

C Both I and II

D Neither I nor II

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7 Doubling which one of the following will double the rate of a first-order reaction?

A Concentration of the reactant

B Size of solid particles

C Volume of solution in which the reaction is carried out

D Activation energy

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8 The reaction

$3M + Q \rightarrow M_3Q$

is first-order with respect to M and second order with respect to Q. When $[M] = 0.100$ mol dm^{-3} and $[Q] = 0.020$ mol dm^{-3}, the rate is 0.010 mol dm^{-3} s^{-1}. What is the value of the rate constant, in mol^{-2} dm^{6} s^{-1}?

A 10

B 100

C 250

D 500

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9 Which statement(s) about the following reaction at 100°C is/are correct?

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

I Every collision between N_2 and H_2 molecules is expected to produce NH_3.

II This reaction must involve a collision between one N_2 and three H_2 molecules.

A I only

B II only

C Both I and II

D Neither I nor II

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10 The mechanism of a reaction is

$XY_2 + XY_2 \rightarrow X_2Y_4$

$X_2Y_4 \rightarrow X_2 + 2Y_2$

$X_2 + Y_2 \rightarrow 2XY$

What is the overall equation for the reaction?

A $X_2Y_4 \rightarrow 2XY_2$

B $2XY_2 \rightarrow X_2 + 2Y_2$

C $2XY_2 \rightarrow 2XY + Y_2$

D $X_2Y_4 \rightarrow 2XY + Y_2$

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 For a reaction between compounds D and E, the rate expression is

rate = $k[D]^2[E]$

Calculate the value of k, including units, for the reaction when the concentrations of both **D** and **E** are 1.35×10^{-2} mol dm^{-3} and the reaction rate is 3.75×10^{-5} mol dm^{-3} min^{-1}.

(3 marks)

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2 The overall equation for a reaction that occurs in two steps is

$P + 2Q \rightarrow R$

The rate expression for the reaction is

Rate = $k[P][Q]$

a Suggest a mechanism for this reaction and identify the rate-determining step.

(2 marks)

b Deduce the molecularity of the reaction.

(1 mark)

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3 In a first-order reaction it takes four minutes for the concentration of a reactant to decrease from 0.08 mol dm^{-3} to 0.04 mol dm^{-3}. Deduce the time for the concentration to decrease from 0.04 mol dm^{-3} to 0.02 mol dm^{-3}.

(1 mark)

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4 The rate constant, $\boldsymbol{k}$, for any reaction is related to the activation energy, $\boldsymbol{E_a}$, by the Arrhenius equation.

Explain the meaning of the terms: *rate constant* and *activation energy*.

(4 marks)

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Part C: Data-based question

Nitrogen(II) oxide reacts with bromine according to the following equation.

$$2NO(g) + Br_2(g) \rightarrow 2NOBr(g) \qquad \Delta H = \text{negative}$$

The data below were obtained for the reaction between NO(g) and Br_2(g) at a specified temperature and pressure.

Experiment	Initial [NO] / mol dm^{-3}	Initial [Br_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	2.00×10^{-2}	5.00×10^{-3}	3.20×10^{-3}
2	2.00×10^{-2}	2.50×10^{-3}	1.60×10^{-3}
3	4.00×10^{-2}	5.00×10^{-3}	1.30×10^{-2}

a Determine, giving a reason, the order of reaction with respect to NO and the order of reaction with respect to Br_2.

(2 marks)

b Derive the rate expression for the reaction between NO and Br_2.

(1 mark)

c Calculate the rate constant for the rate expression using experiment 1 and state its units.

(2 marks)

d If the total volume of the reaction mixture was doubled at constant temperature, state the effect, if any, on

i the rate constant.

(1 mark)

ii the rate of change of the Br_2(g) concentration.

(1 mark)

e Draw a labelled enthalpy level diagram for the reaction between NO(g) and Br_2(g), with and without the use of a catalyst.

(3 marks)

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Part D: Extended-response question

The compound iodine chloride, ICl, reacts with hydrogen to form iodine and hydrogen chloride.

a Deduce the equation for this reaction.

(1 mark)

b The kinetics of this reaction were studied at a certain temperature, when all the reactants and products were in the gas phase. The table shows the initial rate of reaction for different concentrations of reactants.

Experiment	[ICl] mol dm^{-3}	[H_2] / |mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.100	0.0500	5.00×10^{-3}
2	0.200	0.0500	1.00×10^{-2}
3	0.200	0.0250	2.50×10^{-3}

Deduce and explain the order of reaction with respect to ICl and H_2.

(4 marks)

c Write the rate expression for the reaction.

(1 mark)

d Use information from experiment 1 to determine the value, with units, of the rate constant for the reaction.

(2 marks)

e Determine the rate of reaction when the concentrations of reactants in Experiment 1 are both doubled.

(1 mark)

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Total marks: 40

6 EQUILIBRIUM

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 17: Equilibrium.

By the end of this chapter, you should be able to:

- describe the equilibrium established between a liquid and its vapour
- describe how the equilibrium vapour pressure is affected by temperature, and sketch graphs to illustrate the relationship
- explain the relationship between temperature and equilibrium vapour pressure in terms of the kinetic theory
- state and explain the relationship between enthalpy of vaporization, boiling point and the strength of intermolecular forces
- calculate the equilibrium constant for a reaction, given appropriate concentration values or the required data to calculate these
- use an equilibrium constant and concentration data to calculate the concentration of an unknown species
- predict the progress of a reaction to reach equilibrium, given appropriate concentration values prior to the system reaching equilibrium.

IBO Assessment statements 17.1.1 to 17.2.1

Dynamic equilibrium is the term used to describe a reaction in which the forward and the backward reactions are both proceeding and the rate of the forward reaction is equal to the rate of the backward reaction. Both chemical reactions and physical change can reach a state of dynamic equilibrium; in particular, changes of state reach dynamic equilibrium after they have been occurring for a period of time.

Ice cubes in a glass of cold water will maintain a constant size after that water has reached the same temperature as the ice cubes. A half-filled, stoppered bottle of water on a warm day contains water molecules that are constantly in motion, with some escaping the surface of the water and entering the gaseous phase, while water molecules in the air above the surface are colliding with the water surface and being captured back into the liquid state at exactly the same rate. In both the glass of ice water and the bottle of water a state of equilibrium exists between the two states of water:

$$H_2O(s) \rightleftharpoons H_2O(l) \qquad \text{and} \qquad H_2O(l) \rightleftharpoons H_2O(g)$$

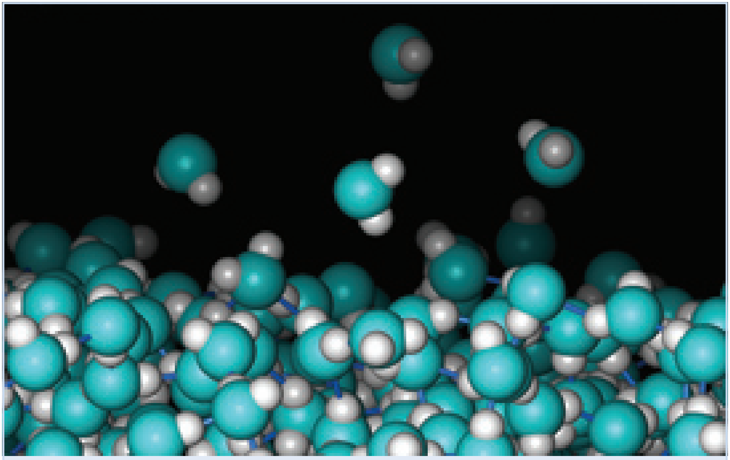


Figure 6.0.1 Liquid water molecules exist in equilibrium with those in the gaseous phase.

6.1 LIQUID–VAPOUR EQUILIBRIUM

AS 17.1.1 **Describe the equilibrium established between a liquid and its own vapour and how it is affected by temperature changes.** © IBO 2007

Let us consider more closely the equilibrium formed between a liquid and its **vapour**. This is known as **phase** equilibrium. A phase is a homogeneous part of a system that is physically distinct from other parts of the system. Solids, liquids and gases are physically distinct from each other by means of their physical structure. In phase equilibrium the first phase (e.g. liquid) is changing into the second phase (e.g. vapour) at the same rate as the vapour is changing into the liquid. Note that the term *vapour* is used to describe a gas that is below its **critical temperature**, the highest temperature at which the vapour can be changed to a liquid by an increase in pressure. For water, the critical temperature is 374°C, so gaseous water below 374°C is correctly called water vapour.

$$\text{liquid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{vapour} \qquad \Delta H \text{ +ve}$$

CHEM COMPLEMENT

Critical temperature and pressure

Under normal conditions, a gas will liquefy if a pressure is applied to it. At 100°C, water vapour will turn back to liquid water at a pressure of 101.3 kPa (1 atm). At higher temperatures, a greater pressure is needed to achieve the same result—143.2 kPa at 110°C and 2.206×10^6 kPa at 374°C. At temperatures above 374°C, no amount of pressure will change gaseous water into liquid water. This value is known as the critical temperature. The gas will become compressed, but it will not change state.

The **critical pressure** is the amount of pressure that is needed to liquefy the gas at the critical temperature. For water, the critical pressure is 2.206×10^6 kPa.

The critical temperature can also be thought of as the highest temperature at which a liquid can exist.

Interactive CW Animation

Liquid–vapour equilibrium

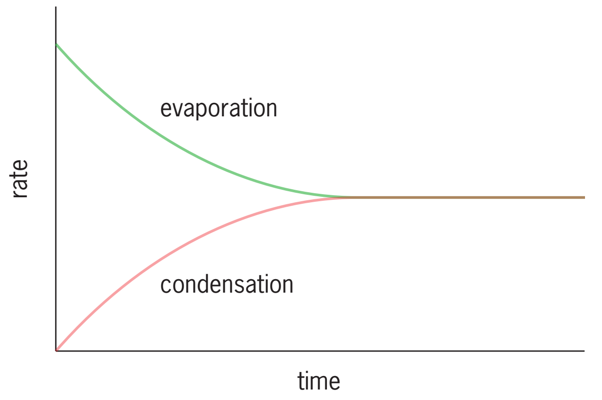


Figure 6.1.1 As the system approaches equilibrium, the rate of evaporation decreases and the rate of condensation increases. At equilibrium, rate of evaporation = rate of condensation.

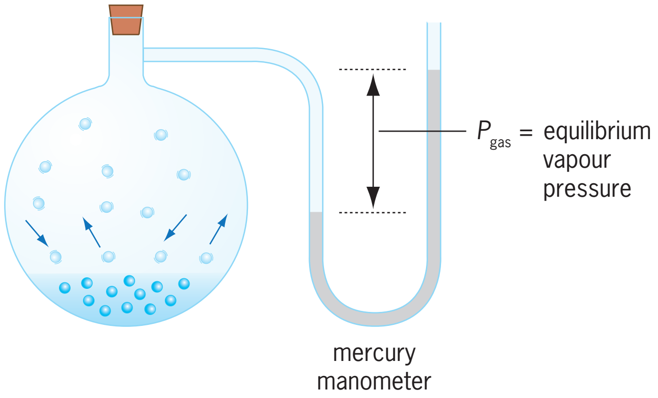


Figure 6.1.2 At equilibrium, molecules enter and leave the liquid at the same rate.

When a liquid evaporates, the gaseous molecules produced exert a vapour pressure. As the number of molecules in the vapour phase increases, the vapour pressure increases. The vapour pressure increases until the system reaches equilibrium, at which point the vapour pressure remains constant. This constant vapour pressure is possible because, as the concentration of molecules in the vapour phase increases, some molecules condense; that is, return to the liquid phase. At equilibrium, the rate of **condensation** is equal to the rate of **evaporation**. The vapour pressure at this point is called the **equilibrium vapour pressure**. It is the maximum vapour pressure of a liquid at a given temperature.

The equilibrium vapour pressure is constant at a constant temperature and increases as the temperature increases for a given system. Note that the equilibrium vapour pressure is independent of both the volume and the surface area of the liquid.

AS 17.1.2
Sketch graphs showing the relationship between vapour pressure and temperature, and explain them in terms of the kinetic theory. © IBO 2007

The relationship between equilibrium vapour pressure and temperature can clearly be seen in a graph. As the temperature increases, the vapour pressure initially increases only slightly, but as the boiling point is approached, the graph becomes steeper and the increase is more dramatic. A liquid with a high vapour pressure at a given temperature is said to be **volatile**—it evaporates rapidly from an open dish. Propanone is the most volatile liquid represented in figure 6.1.3.

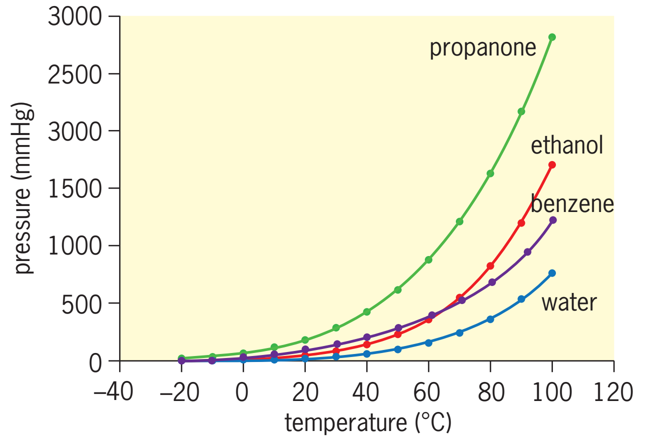


Figure 6.1.3 For a given system, as the temperature increases, the equilibrium vapour pressure increases.

The amount of energy required to break the bonds between molecules in the liquid phase depends on the strength of the intermolecular bonding. This can be seen clearly in figure 6.1.3 in which the equilibrium vapour pressures of ethanol, water, benzene and propanone are plotted against temperature. The intermolecular forces between water molecules—hydrogen bonding—are the strongest of these four substances, subsequently water has the lowest vapour pressure at 100°C. Propanone, a smaller molecule than benzene, is a polar molecule with dipole–dipole attraction between its molecules. Ethanol is a polar molecule with dipole–dipole attraction and hydrogen bonding between its molecules. The strength of the intermolecular forces between the propanone molecules is weaker than that between ethanol molecules, so the vapour pressure for propanone is greater at 100°C than for any of the other substances.

As the temperature increases, the distribution of molecular kinetic energies within the liquid changes (*Chemistry: For use with the IB Diploma Programme Standard Level*, section 7.2). At a higher temperature, a greater proportion of molecules have a greater kinetic energy than they do at lower temperatures. As a result, a greater proportion of molecules have sufficient energy to overcome the intermolecular forces in the liquid and join the vapour phase. This results in a greater equilibrium vapour pressure for a given substance at higher temperatures than at lower temperatures.

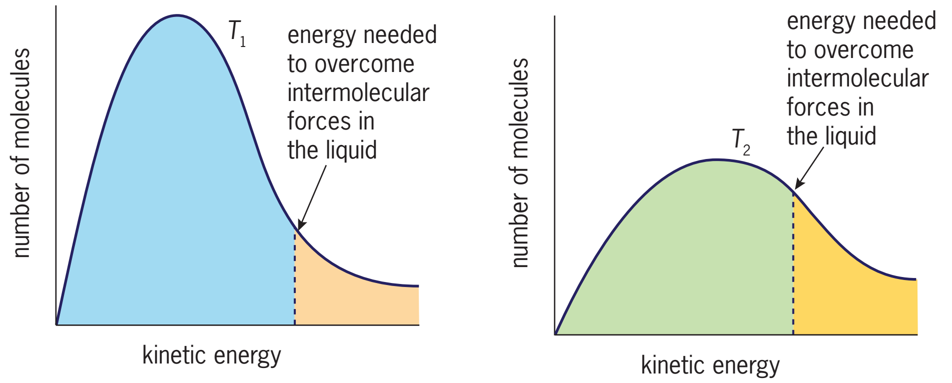


Figure 6.1.4 The proportion of molecules with sufficient energy to overcome the intermolecular forces in the liquid is greater at the higher temperature T_2.

WORKSHEET 6.1
Vapour pressures

Equilibrium vapour pressure

Enthalpy of vaporization

AS 17.1.3 State and explain the relationship between enthalpy of vaporization, boiling point and intermolecular forces. © IBO 2007

The **enthalpy of vaporization**, ΔH_{vap}, is the amount of energy required to vaporize one mole of a liquid. As discussed earlier, in order to vaporize a liquid, the intermolecular forces between the molecules of the liquid must be broken. If the intermolecular attraction is strong, such as the hydrogen bonding between water molecules, a lot of energy will be needed to free the molecules from the liquid phase. Similarly, if there are only weak van der Waals' forces between the molecules, little energy will be needed to achieve vaporization. This leads us to generalize that the stronger the intermolecular forces between the molecules of a liquid, the greater will be the enthalpy of vaporization.

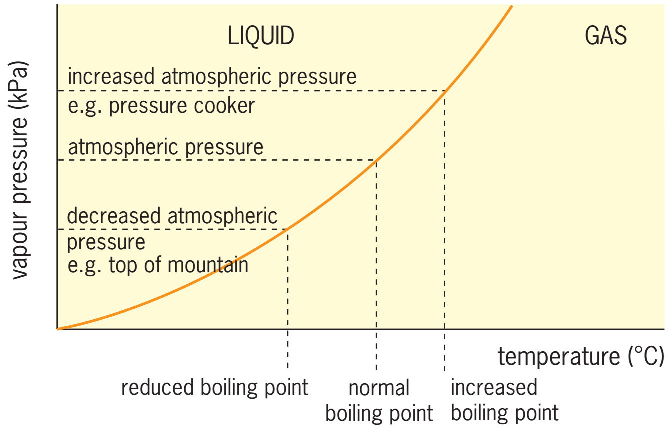


Figure 6.1.5 The temperature at which the vapour pressure of a liquid is equal to 101.3 kPa (1 atm) pressure is called the normal boiling point of the liquid.

The **boiling point** of a liquid is the temperature at which the vapour pressure of the liquid is equal to the external pressure. The normal boiling point of a liquid is the temperature at which it boils when the external pressure is 1 atm. When a liquid is boiling, its temperature remains constant. This is because the energy being supplied to the liquid is used to produce molecules with enough energy to escape the liquid phase and join the vapour phase. The average kinetic energy of the molecules remaining in the liquid phase is constant, so the temperature does not change.

TABLE 6.1.1 ENTHALPIES OF VAPORIZATION AND BOILING POINTS FOR SELECTED LIQUIDS

Substance	Enthalpy of vaporization, ΔH_{vap} (kJ mol^{-1})	Boiling point (°C)
Mercury	59.0	357
Water	40.8	100
Benzene	31.0	80.1
Ethanol	39.3	78.3
Propanone	31.0	56.0

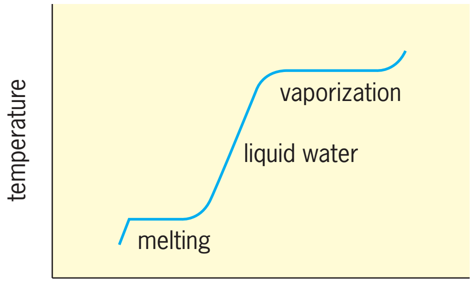


Figure 6.1.6 As energy is added to a sample of water, the temperature increases, except at the times when a change of state is occurring.

To see the connection between enthalpy of vaporization, ΔH_{vap}, boiling point and intermolecular forces, let us consider the changes that occur as a liquid is heated.

As the liquid is heated, its temperature increases and the molecules of the liquid move with increasing energy. We saw earlier that the proportion of molecules that are in the vapour phase increases with temperature and the equilibrium vapour pressure also increases (see figure 6.1.3). When the equilibrium vapour pressure is equal to the external pressure over the liquid (usually 1 atm pressure), the liquid boils. The temperature at which this occurs is the boiling point. The energy that is required for this transition (boiling) to occur is called the enthalpy of vaporization.

Since the strength of intermolecular forces governs the amount of energy needed to break bonds between the molecules of a liquid, the boiling point and the enthalpy of vaporization both increase as the strength of the intermolecular forces increases.

For example, mercury and water are both liquids at room temperature. The bonding between mercury atoms is metallic bonding, while that between water molecules is hydrogen bonding. Although hydrogen bonding is the strongest type of intermolecular force, metallic bonding is more strictly an intramolecular force and as such is stronger. In table 6.1.1 we can see that the boiling point of mercury is 357°C and its enthalpy of vaporization is 59.0 kJ mol^{-1}, while the boiling point of water is 100°C and its enthalpy of vaporization is 40.8 kJ mol^{-1}. With its stronger intermolecular forces, mercury has a higher enthalpy of vaporization and a higher boiling point than water.

THEORY OF KNOWLEDGE

Why do we believe the claims made by scientists? Usually we believe something because we have a good reason or a justification for doing so. We tend to agree more with scientific claims because the justification used involves sound reasoning and empirical observation. Consider, for example, the explanations given for the relationship between the enthalpy of vaporization and the strength of the intermolecular forces between molecules. You accept the reasoning because you can figure it out logically; it makes sense considering what you know. You find further justification by designing an experiment to test the idea and find that, as expected, more heat energy is required to vaporize water, with its stronger intermolecular forces, than propanone.

- If we are more likely to believe knowledge claims that are justified by reasoning or empirical observation, what sorts of justification are we less likely to believe?
- Can you think of anything you have heard or read in Chemistry that seemed so outrageous that you found it hard to believe? What made it so hard to believe?
- Comment on the claim 'We tend to agree more with scientific claims because the justification used involves sound reasoning and observation.' Are you more likely to believe the claims made in Chemistry than those made in your other subjects? Explain.
- Identify the following arguments as either inductive or deductive reasoning.
  1. Alcohol A absorbs heat energy when it vaporizes. Alcohol B absorbs heat energy when it vaporizes. Alcohol C absorbs heat energy when it vaporizes. Therefore all alcohols absorb heat energy when they vaporize.
  2. All alcohols absorb heat energy when they vaporize. A is an alcohol; therefore, A absorbs heat energy when it vaporizes.

CHEM COMPLEMENT

Boiling temperature and pressure

Figure 6.1.7 A pressure cooker cooks foods at pressures above atmospheric pressure and the resulting higher boiling temperature of the water inside decreases cooking time considerably.

Most of us have never boiled water on top of a high mountain; however, it is well known that the atmospheric pressure at the top of a high mountain is lower than that at sea level. On top of Mt Everest, the tallest mountain in the world, water boils at only 69.57°C! Since the boiling temperature is the temperature at which the vapour pressure of a liquid is equal to the external pressure, the lower external pressure on top of Mt Everest of 0.302 atm (30.6 kPa) is easily matched by the vapour pressure as the water is heated, so water boils at a much lower temperature than at sea level.

Under conditions of high pressure, the boiling point of water (and other liquids) is greater than normal. This is the basis on which pressure cookers work. When cooking commences, the pressure is increased inside the strongly built pressure cooker and the small amount of water inside the cooker boils at a temperature above 100°C. This higher temperature increases the rate at which the food cooks, producing a speedy meal!

Section 6.1 Exercises

1 Define the term *equilibrium vapour pressure*.

2 Describe the processes that are occurring when the equilibrium vapour pressure has been reached at a given temperature.

3 Consider the following boiling points.

Liquid	Ethanol	Water	Ethoxyethane
Boiling point (°C)	78	100	35

List these three liquids in order of increasing equilibrium vapour pressures at 20°C and explain the order that you have chosen.

4 Explain how the equilibrium vapour pressure depends on the:

a temperature

b intermolecular forces in the liquid

c volume of the liquid.

5 Sketch a graph to show the relationship between the equilibrium vapour pressure and temperature of a volatile liquid X.

6 Considering equilibrium vapour pressure, explain the following observation:

Wet clothes dry more quickly on a hot dry day than on a hot, humid day.

7 Heat energy must be supplied to boil a liquid. Explain what happens to this heat energy.

8 **a** Explain, in terms of kinetic theory, why for any given liquid the vapour pressure is greater at high temperatures than at low temperatures.

b Draw two Maxwell–Boltzmann curves to illustrate your answer to part **a**.

9 What can be understood about the intermolecular forces in a liquid from its enthalpy of vaporization?

10 The enthalpy of vaporization, for four liquids, W, X, Y and Z are as follows.

Liquid	W	X	Y	Z
Enthalpy of vaporization, ΔH_{vap} (kJ mol^{-1})	40.5	32.4	38.2	41.1

a Deduce the order of increasing boiling points for these four liquids.

b Compare the intermolecular forces present in liquids X and Z.

6.2 THE EQUILIBRIUM LAW

Many chemical reactions proceed to a very large extent, effectively proceeding to completion. For these reactions, the assumption that all the reactants are completely converted to products is valid, and stoichiometric calculations based on this premise are accurate. For those reactions that proceed to a lesser extent, scientists require some way of quantifying their results so that calculations of product yield can be made.

The French chemist Claude Berthollet (1748–1822) showed that the concentration of reactants in an equilibrium system had a direct effect on the concentration of products formed. This work led two Norwegian chemists, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900), to look more closely at the relationship between masses of reactants and products in reactions. After conducting numerous experiments, they were to propose in 1864 what came to be known as the equilibrium law.

Their calculations showed that there was a mathematical relationship between the concentrations of the products formed in a reaction once equilibrium had been reached and the concentrations of the reactants left behind. The coefficients of the species involved in the equation were important, as was the temperature at which the reaction proceeded. Guldberg and Waage determined that for the general reaction:

$$aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$$

at constant temperature, the concentrations of reactants and products are related by the ratio:

$$K_c = \frac{[P]^p[Q]^q\ldots}{[A]^a[B]^b\ldots}$$

where K_c is the equilibrium constant for the reaction at a specified temperature.

In chapter 8 of *Chemistry: For use with the IB Diploma Programme Standard Level*, you studied a range of equilibrium systems and their equilibrium constant expressions. In order to revise that work, some examples of equilibrium constant expressions and their units are given below.

Worked example 1

Write the equilibrium constant expression, K_c, and state the units for each of the following equilibria.

a $Cu^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons CuCl_4{}^{2-}(aq)$

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

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

Solution

a $K_c = \dfrac{[CuCl_4{}^{2-}]}{[Cu^{2+}][Cl^-]^4}$

Units: $\dfrac{\cancel{mol}\ \cancel{dm^{-3}}}{\cancel{mol}\ \cancel{dm^{-3}} \times mol^4\ dm^{-12}} = mol^{-4}\ dm^{12}$

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

Units: $\dfrac{\cancel{mol^2}\ \cancel{dm^{-6}}}{\cancel{mol^2}\ \cancel{dm^{-6}}} =$ no units

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

Units: $\dfrac{mol^{\cancel{2}1}\ dm^{\cancel{-6}-3}}{\cancel{mol}\ \cancel{dm^{-3}}} = mol\ dm^{-3}$

Calculating the value of the equilibrium constant K_c

17.2.1
Solve homogeneous equilibrium problems using the expression for K_c. © IBO 2007

A homogeneous equilibrium system is one in which all the reactants and products are in the same state. For example, the equilibrium

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

is a homogeneous equilibrium system.

For a system at equilibrium, the equilibrium constant expression has a constant value at a particular temperature, no matter what the initial concentrations of reactant and product species may be.

The magnitude of the equilibrium constant indicates the extent of a chemical reaction; the larger the value, the further to the right the reaction will proceed and so the more product that is formed.

If $K_c >> 1$, the reaction goes almost to completion.
If $K_c << 1$, the reaction hardly proceeds.

PRAC 6.1
Determination of an equilibrium constant

Equilibrium constants have an extraordinary range—from as small as 10^{-40} to as large as 10^{40}! Importantly, the constant can never be zero; all reactions proceed to at least some extent, even if only negligibly. The dependence of the equilibrium constant on temperature means that the temperature must always be quoted when a certain value of K_c for a reaction is quoted.

TABLE 6.2.1 EQUILIBRIUM CONSTANTS OF SOME COMMON REACTIONS

Reaction	Temperature (°C)	Equilibrium constant, K_c
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	25	1×10^{-30}
$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$	25	6.8×10^{-4}
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	100	0.211
$2NO_2(g) \rightleftharpoons N_2O_4(g)$	100	4.72
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	300	9.60
$CO(g) + Cl_2(g) \rightleftharpoons COCl_2$	100	4.56×10^9

To actually determine the equilibrium constant for a particular reaction, experimental data providing the concentrations of all species involved at equilibrium is required. To obtain an accurate value, more than one set of data should be used, so that an average equilibrium constant value can be calculated. An example of such a set of experimental data and calculations is provided below.

The reaction representing the industrial production of ammonia is:

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

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}\ \text{mol}^{-2}\ \text{dm}^6$$

TABLE 6.2.2 EQUILIBRIUM CONSTANT CALCULATION FOR THE REACTION $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ AT 280°C

Experiment number	Equilibrium concentrations (mol dm^{-3})			$\frac{[NH_3]^2}{[N_2][H_2]^3}$
	$[N_2]$	$[H_2]$	$[NH_3]$	
1	0.0500	0.0500	0.00106	0.180
2	0.0890	0.116	0.00497	0.178
3	0.350	0.482	0.0840	0.180
4	0.161	0.372	0.0385	0.179

To determine the equilibrium constant values shown in the right-hand column of table 6.2.2, a calculation such as the one below is carried out. Notice that the concentrations for each product and reactant are substituted into the equilibrium constant expression and are raised to the appropriate power.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.00106)^2}{0.0500 \times (0.0500)^3} = \frac{1.123 \times 10^{-6}}{6.25 \times 10^{-6}} = 0.180\ \text{mol}^{-2}\ \text{dm}^6$$

When experiments 1 to 4 are all considered, the average equilibrium constant for this reaction at 280°C is found to be 0.179 $\text{mol}^{-2}\ \text{dm}^6$.

Worked example 2

Calculate the equilibrium constant for the reaction:

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)\ \text{at } 20°C$$

given that the equilibrium concentrations of the species involved are:

$[PCl_3] = 1.50 \times 10^{-3}\ \text{mol dm}^{-3}$, $[Cl_2] = 8.25 \times 10^{-2}\ \text{mol dm}^{-3}$
$[PCl_5] = 1.67\ \text{mol dm}^{-3}$

Solution

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{1.67}{(1.50 \times 10^{-3}) \times (8.25 \times 10^{-2})} = 1.35 \times 10^4\ \text{mol}^{-1}\ \text{dm}^3$$

Worked example 3

Calculate the equilibrium concentration of $Ag^+(aq)$ ions given the following:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$$

$$K_c = 1.60 \times 10^4 \text{ mol}^{-2} \text{ dm}^6 \text{ at } 25°\text{C}, [NH_3] = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[Ag(NH_3)_2{}^+] = 0.401 \text{ mol dm}^{-3}$$

Solution

$$K_c = \frac{\left[Ag(NH_3)_2{}^+\right]}{[Ag^+][NH_3]^2} = 1.60 \times 10^4 \text{ mol}^{-2} \text{ dm}^6$$

$$[Ag^+] = \frac{\left[Ag(NH_3)_2{}^+\right]}{\left[NH_3\right]^2 \times (1.60 \times 10^4)} = \frac{0.401}{(5.00 \times 10^{-3})^2 \times (1.60 \times 10^4)} = 1.00 \text{ mol dm}^{-3}$$

CHEM COMPLEMENT

Competing equilibria: dissolving a precipitate

It is quite common for two or more reactions to occur at the same time, and where these reactions involve the same reactant/s, we say they are ‘competing equilibria’. This competition for an ion can be very useful in dissolving precipitates. Let us consider the reaction between silver ions, Ag^+, and chloride ions, Cl^-, to produce the precipitate silver chloride, AgCl. The solubility product, $K_{sp} = [Ag^+][Cl^-]$ ([AgCl] is excluded because it is a solid substance) for the reverse reaction is very small, which is to be expected, since AgCl is considered an insoluble salt.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

The addition of aqueous ammonia, $NH_3(aq)$, to the solution containing the AgCl precipitate creates a second equilibrium

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq) \qquad K_{st} = 1.7 \times 10^7 \text{ mol}^2 \text{ dm}^{-6}$$

where $K_{st} = \dfrac{\left[Ag(NH_3)_2{}^+\right]}{\left[Ag^+\right]\left[NH_3\right]^2}$ and is called the stability constant.

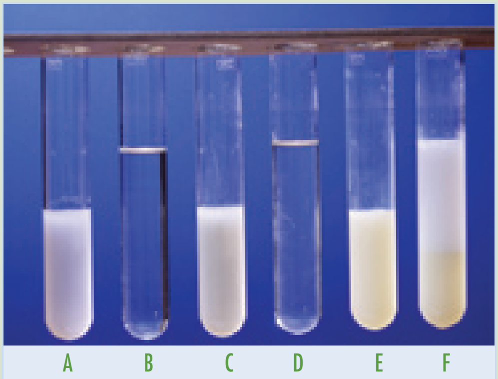


Figure 6.2.1 Silver chloride (A) and silver bromide (C) dissolve in concentrated ammonia but silver iodide (E) does not. Notice the different colours of the halide compounds: silver chloride is white, silver bromide is cream and silver iodide is light yellow.

Since the equilibrium between Ag^+ and NH_3 has such a large equilibrium constant, the ammonia reacts with the small amount of Ag^+ in solution, easily forming $Ag(NH_3)_2{}^+$. According to Le Chatelier’s principle, the removal of some $Ag^+(aq)$ from the first equilibrium pushes it towards the right, making more products and starting to dissolve the precipitate of AgCl. This continues and the diammine silver(I) complex forms until all of the AgCl has completely dissolved.

This series of reactions can be used in the identification of halide ions in precipitates. Silver chloride (white) dissolves in dilute ammonia, while silver bromide (cream) dissolves in concentrated ammonia and silver iodide (yellow) does not even dissolve in concentrated ammonia.

WORKSHEET 6.2
Equilibrium constant calculations

Further equilibrium constant calculations

In some cases you might know the initial concentrations of the reactants and will need to find the value of the equilibrium constant, or perhaps a concentration of a reactant at equilibrium. Because substitution of values into the equilibrium constant expression will only result in a value for the equilibrium constant for an equation when the concentrations used are actually at equilibrium, the concentrations of reactants and products at equilibrium must be determined before they can be used to find the equilibrium constant.

Worked example 4

Some N_2O_4 was introduced into an evacuated 5.0 dm^3 vessel at a temperature of 25°C. The gas dissociated according to the equation below:

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

The gases were left to reach equilibrium.

Once equilibrium was reached, the concentrations of N_2O_4 and NO_2 were 0.077 mol dm^{-3} and 0.019 mol dm^{-3} respectively. Calculate the equilibrium constant for the reaction at 25°C.

Solution

$$[N_2O_4]_{eq} = 0.077 \text{ mol dm}^{-3} \text{ and } [NO_2]_{eq} = 0.019 \text{ mol dm}^{-3}$$

$$\therefore \text{ equilibrium constant } K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.019^2}{0.077} = 4.7 \times 10^{-3} \text{ mol dm}^{-3}$$

More complex equilibrium constant calculations may require us to use the principles of stoichiometry to determine how much product has been formed and/or reactant consumed before the equilibrium concentrations can be determined. For problems of this nature, it is useful to draw a simple table. The value of such a table is that it can be used for almost all problems of this type and it makes it easy to keep track of the calculations as they proceed. The table template is shown below.

Volume of reaction vessel (dm^3)	Reactants	Products
	Names of reactants	Names of products
Molar ratio in the equation		
Initial amount of substance, n_i (mol)		
Change (mol)		
Amount of substance at equilibrium, n_{eq} (mol)		
Concentration at equilibrium, $[\ ]_{eq}$ (mol dm^{-3})		

When you use this table template, you should write in the actual value of the volume and the actual formulas of the reactants and products. This will help you stay focused on the question at hand, and is a useful way to process the information in the question.

Worked example 5

4.00 mol of HI(g) was admitted to an evacuated 2.00 dm^3 reaction vessel and allowed to reach equilibrium at a constant temperature, according to the equation:

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

At equilibrium, 0.250 mol of I_2 had formed.

a Determine the equilibrium concentrations of all species at this temperature.

b Calculate the equilibrium constant for the reaction.

Solution

a To solve the problem, first draw the table.

Volume = 2.00 dm^3	Reactants	Products	
	HI	H_2	I_2
Molar ratio			
n_i (mol)			
Change (mol)			
n_{eq} (mol)			
$[\ ]_{eq}$ (mol dm^{-3})			

Step 1: The molar ratio is given in the equation. The vessel was ‘evacuated’, or empty, at the start of the reaction and 4.00 mol of HI was added. Once equilibrium had been reached, 0.250 mol of I_2 had formed. Add this information to the table.

Volume = 2.00 dm^3	Reactants	Products	
	HI	H_2	I_2
Molar ratio	2	1	1
n_i (mol)	4.00	0	0
Change (mol)			
n_{eq} (mol)			0.250
$[\ ]_{eq}$ (mol dm^{-3})			

Step 2: Add the changes that must have happened between the initial conditions and those at equilibrium. In this case, the amount of iodine had increased by 0.250 mol. From the equation provided, the hydrogen must also have increased by the same quantity (1 : 1 ratio) and the amount of hydrogen iodide must have decreased by twice as much (2 : 1 ratio).

Volume = 2.00 dm^3	Reactants	Products	
	HI	H_2	I_2
Molar ratio	2	1	1
n_i (mol)	4.00	0	0
Change (mol)	−0.500	+0.250	+0.250
n_{eq} (mol)			0.250
$[\ ]_{eq}$ (mol dm^{-3})			

Step 3: Simple arithmetic enables the calculation of the number of mole of each reactant and product at equilibrium by incorporating the number of mole initially and the amount of change. The concentration at equilibrium is determined using the volume that you have recorded in your table ($c = \frac{n}{V}$) and you are now in a position to calculate the equilibrium constant.

Volume = 2.00 dm^3	**Reactants**	**Products**	
	HI	**H_2**	**I_2**
Molar ratio	2	1	1
n_i (mol)	4.00	0	0
Change (mol)	−0.500	+0.250	+0.250
n_{eq} (mol)	4.00 − 0.500 = 3.50	0 + 0.250 = 0.250	0.250
[ ]$_{eq}$ (mol dm^{-3})	$\frac{3.50}{2.00} = 1.75$	$\frac{0.250}{2.00} = 0.125$	$\frac{0.25}{2.00} = 0.125$

b This part of the question is now straightforward since all the values of [ ]$_{eq}$ are known:

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.125 \times 0.125}{(1.75)^2} = 5.10 \times 10^{-3} \text{ (no units)}$$

Worked example 6

1.800 mol of ammonia is introduced into an evacuated 5.00 dm^3 vessel and allowed to come to equilibrium. The concentration of nitrogen at equilibrium was determined to be 0.0435 mol dm^{-3}. Calculate the equilibrium constant for the reaction shown below, given that the temperature remained constant at 160°C throughout.

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

Solution

Step 1: Record all known information in the table. Note that the reaction has been written in the reverse order to that which is most common. The reactants must still be regarded as those formulas that appear on the left-hand side of the arrow and products are those formulas that appear on the right-hand side of the arrow.

Volume = 5.00 dm^3	**Reactants**	**Products**	
	NH_3	**N_2**	**H_2**
Molar ratio	2	1	3
n_i (mol)	1.800	0	0
Change (mol)			
n_{eq} (mol)			
[ ]$_{eq}$ (mol dm^{-3})		0.0435	

Step 2: In this case, the concentration of N_2 at equilibrium is known, so use the volume to determine the amount in mol of N_2 ($n = cV$). Use this information and the reaction equation to determine the changes that must have occurred as the reaction proceeded.

Volume = 5.00 dm^3	**Reactants**	**Products**	
	NH_3	**N_2**	**H_2**
Molar ratio	2	1	3
n_i (mol)	1.800	0	0
Change (mol)	$-(2 \times 0.2175) = -0.435$	$+ 0.2175$	$+(3 \times 0.2175) = + 0.6525$
n_{eq} (mol)		$0.0435 \times 5.00 = 0.2175$	
$[\ ]_{eq}$, (mol dm^{-3})		0.0435	

Step 3: Complete the table and so calculate the equilibrium constant.

Volume = 5.00 dm^3	**Reactants**	**Products**	
	NH_3	**N_2**	**H_2**
Molar ratio	2	1	3
n_i (mol)	1.800	0	0
Change (mol)	$-(2 \times 0.2175) = -0.435$	$+ 0.2175$	$+(3 \times 0.2175) = + 0.6525$
n_{eq} (mol)	$1.800 - 0.435 = 1.365$	$0.0435 \times 5.00 = 0.2175$	$0 + 0.6525 = 0.6525$
$[\ ]_{eq}$ (mol dm^{-3})	$\frac{1.365}{5.00} = 0.273$	0.0435	$\frac{0.6525}{5.00} = 0.131$

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{0.0435 \times (0.131)^3}{(0.273)^2} = \frac{9.78 \times 10^{-5}}{0.0745} = 1.31 \times 10^{-3} \text{ mol dm}^{-3}$$

To determine whether a system has reached equilibrium, measurements of the concentrations of reactants and products can be taken at intervals of time and substituted into the equilibrium constant expression. When the system is not at equilibrium, this expression may be called the concentration fraction. The value of the concentration fraction will change as the system is approaching equilibrium and will become constant (and equal to the equilibrium constant) at equilibrium.

If the value of the concentration fraction is increasing, then the system is moving in the forward direction (towards the right) and more products are being made in order to reach equilibrium. If the value of the concentration fraction is decreasing, then the system is moving in the backward direction (towards the left) and more reactants are being made as equilibrium is approached.

Worked example 7

0.0900 mol of N_2O_4 and 0.196 mol of NO_2 were introduced into an evacuated 2.0 dm^3 vessel at a temperature of 30°C. The gases were allowed to come to equilibrium at this temperature according to the equation:

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

Once equilibrium was reached, the concentrations of N_2O_4 and NO_2 were 0.0775 mol dm^{-3} and 0.0655 mol dm^{-3} respectively.

a Determine the initial concentration fraction for the reaction system.

b Calculate the equilibrium constant, K_c, for the reaction at 30°C.

c In which direction did the reaction proceed to reach equilibrium?

Solution

a To determine the concentration fraction, we must first calculate the initial concentrations of N_2O_4 and NO_2:

$$[N_2O_4]_i = \frac{n}{V} = \frac{0.0900}{2.00} = 0.0450 \text{ mol dm}^{-3} \text{ and}$$

$$[NO_2]_i = \frac{n}{V} = \frac{0.196}{2.00} = 0.0980 \text{ mol dm}^{-3}$$

The concentration fraction has the same formula as the equilibrium constant, but uses concentrations that are not necessarily at equilibrium:

$$\text{Concentration fraction} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0980)^2}{0.0450} = 0.213 \text{ mol dm}^{-3}$$

b $[N_2O_4]_{eq} = 0.0775 \text{ mol dm}^{-3}$ and $[NO_2]eq = 0.0655 \text{ mol dm}^{-3}$

$$\therefore K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0655)^2}{0.0775} = 0.0554 \text{ mol dm}^{-3}$$

c As the value of the equilibrium constant was smaller than the initial concentration fraction, to reach equilibrium the reaction must have proceeded to the left to produce more reactant and consume some of the product. When the concentrations of N_2O_4 and NO_2 at equilibrium are compared with their initial values, this is clearly the case.

Worked example 8

The equilibrium between nitrogen monoxide and bromine is represented by the equation

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g) \qquad K_c = 2.0 \text{ at } 298 \text{ K}$$

a Write the equilibrium constant expression, K_c.

b Deduce the units for the equilibrium constant, K_c.

c 1.5 mole of NO(g), 1.5 mole of $Br_2(g)$ and 2.0 mole of NOBr(g) were placed in an empty 1 dm^3 container and allowed to come to equilibrium at 298 K. Predict whether the equilibrium mixture would contain more or less than 1.5 mole of NO(g).

Solution

a $K_c = \dfrac{[NOBr]^2}{[NO]^2[Br_2]} = 2.0$ at 298 K

b Units: $\dfrac{mol^2\ dm^{-6}}{mol^3\ dm^{-9}} = mol^{-1}\ dm^3$

c First we must find the value of the concentration fraction for the initial conditions:

Concentration fraction $= \dfrac{[NOBr]^2}{[NO]^2[Br_2]} = \dfrac{2.0^2}{1.5^2 \times 1.5} = \dfrac{4.0}{3.375} = 1.19\ mol^{-1}\ dm^3$

Since the value of the concentration fraction is less than that of the equilibrium constant, the reaction must proceed in the forward direction, making more products and using up reactants in order to reach equilibrium.

There will be less than 1.5 mole of NO(g) at equilibrium.

……

Section 6.2 Exercises

1 The table below provides experimental data, at 450°C, for the determination of an equilibrium constant for the reaction:
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 450°C

Experiment number	Equilibrium concentrations (mol dm^{-3})		
	H_2	I_2	HI
1	0.0077	0.0031	0.0334
2	0.0092	0.0022	0.0308
3	0.0086	0.0086	0.0586

a Write an equilibrium constant expression for this reaction.

b Calculate the value of the equilibrium constant for the three sets of experimental data and so determine the average value of K_c.

2 When dissolved in water, triiodide ions, I_3^-, form an equilibrium system with iodine and iodide ions.

$I_3^-(aq) \rightleftharpoons I_2(aq) + I^-(aq)$

In an equilibrium mixture at 300 K, the concentrations of the three ions are as follows:

$[I_3^-] = 0.835\ mol\ dm^{-3}$, $[I_2] = 0.00262\ mol\ dm^{-3}$ and $[I^-] = 0.0307\ mol\ dm^{-3}$

Calculate the value of the equilibrium constant for this reaction at 300 K.

3 A mixture of hydrogen and bromine gases are introduced into a vessel at 220°C and allowed to come to equilibrium according to the equation:

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $\quad K_c = 0.350\ mol^{-1}\ dm^3$ at 220°C

Calculate the concentration of bromine in the container, given that the concentrations of hydrogen and hydrogen bromide are $0.371\ mol\ dm^{-3}$ and $0.115\ mol\ dm^{-3}$ respectively.

4 A mixture of hydrogen iodide and oxygen gas comes to equilibrium in a sealed vessel according to the equation:

$4HI(g) + O_2(g) \rightleftharpoons 2H_2O(g) + I_2(g) \quad K_c = 515\ mol^{-2}\ dm^6$ at 640°C

Calculate the equilibrium concentration of HI, given that the equilibrium concentrations of the other gases present are:

$[H_2O] = 0.663\ mol\ dm^{-3}$, $[I_2] = 0.109\ mol\ dm^{-3}$ and $[O_2] = 0.0726\ mol\ dm^{-3}$

5 0.40 mol of PCl_3 and 0.65 mol of Cl_2 are placed into an empty 10.0 dm^3 vessel at 25°C and allowed to come to equilibrium, according to the equation:

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

When equilibrium is established at 25°C there is 0.55 mol of Cl_2 remaining. Determine the equilibrium concentrations of all three species in the container and so calculate the equilibrium constant at 25°C.

6 0.836 mol of NO_2 and the same amount of N_2O_4 are placed into an evacuated 3.6 dm^3 vessel. At equilibrium, the concentration of NO_2 in the vessel is 0.113 mol dm^{-3}. Determine the equilibrium constant for the equation:

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

7 Consider the gaseous system represented by the equation:

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

0.25 mol of SO_2 and 0.35 mol of NO_2 are added to an evacuated 10.0 dm^3 vessel. When equilibrium is reached at 300°C, the concentration of NO is determined to be 0.0224 mol dm^{-3}. Determine the equilibrium concentrations of the other three gases present and so calculate the equilibrium constant.

8 0.600 mol of HOCl was introduced into an evacuated 3.00 dm^3 vessel at 60°C, where it decomposed to Cl_2O and H_2O according to the equation:

$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$

When equilibrium was reached, 0.489 mol of HOCl remained in the vessel. Determine the equilibrium concentrations of all three gases present and so calculate the equilibrium constant at 60°C.

9 5.80 mol of $N_2(g)$ and 8.20 mol of $H_2(g)$ were mixed in a 4.0 dm^3 vessel and reacted according to the equation:

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

When equilibrium was reached at 350°C, it was found that 0.40 mol of $NH_3(g)$ had been formed. Calculate the value of the equilibrium constant at 350°C.

10 A mixture of 0.200 mol of CO_2, 0.300 mol of H_2 and 0.160 mol of H_2O is placed in a 2.00 dm^3 vessel. The mixture reaches the following equilibrium at 500 K:

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

At equilibrium the concentration of CO(g) is 0.0650 mol dm^{-3}.

a State the equilibrium constant expression for this reaction.

b Calculate the value of the equilibrium constant at 500 K.

Chapter 6 Summary

Terms and definitions

Boiling point The temperature at which the vapour pressure of a liquid is equal to the external pressure.

Condensation The process in which a gas is changed into a liquid.

Critical temperature The highest temperature at which the vapour can be changed to a liquid by an increase in pressure.

Critical pressure The amount of pressure that is needed to liquefy the gas at the critical temperature.

Enthalpy of vaporization, ΔH_{vap} The amount of energy required to vaporize one mole of a liquid.

Equilibrium law The mathematical relationship between the concentrations of products formed in a reaction once equilibrium had been reached and the concentrations of the reactants left behind:

$K_c = \frac{[P]^p[Q]^q\ldots}{[A]^a[B]^b\ldots}$ where a, b, p, q are the coefficients of the reactants and products in the equation for the reaction.

Equilibrium vapour pressure The vapour pressure measured when a dynamic equilibrium exists between condensation and evaporation.

Evaporation The process in which a liquid is transformed into a gas.

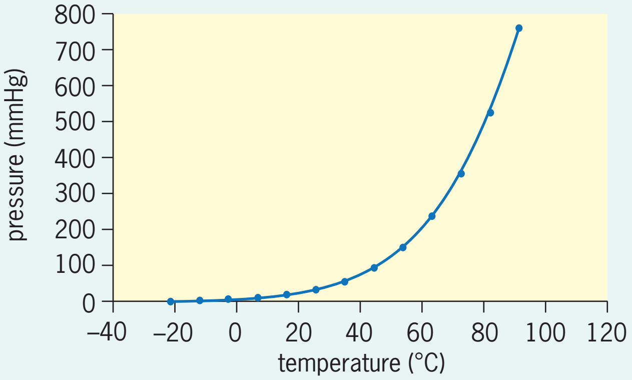
Phase A homogeneous part of a system that is physically distinct from other parts of the system.

Vapour Describes a gas that is below its critical temperature.

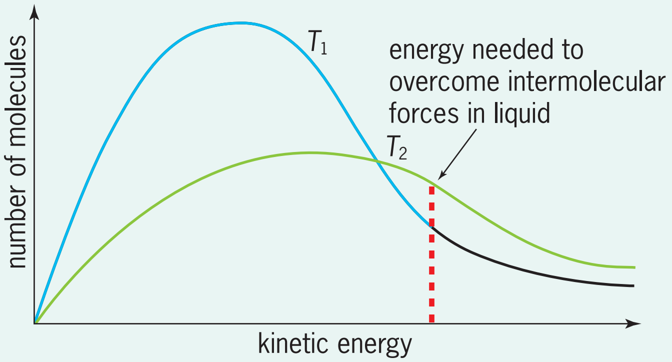
Volatile Evaporates readily from an open dish at room temperature.

Concepts

- As the temperature of a liquid increases, the number of molecules with sufficient kinetic energy to escape the liquid and become vapour increases.
- In a closed system, as the temperature of a liquid increases, the vapour pressure increases.
- In an evacuated container, the vapour pressure will increase as the liquid evaporates and after a while the vapour will start to condense. The equilibrium vapour pressure is reached when the rate of evaporation is equal to the rate of condensation.
- At any given temperature the equilibrium vapour pressure will be constant.
- Graphs show the relationship between equilibrium vapour pressure and temperature.



- The proportion of molecules with sufficient kinetic energy to overcome the intermolecular forces in the liquid and to join the vapour phase increases as temperature increases. This results in a greater equilibrium vapour pressure for a given substance at higher.



- When the equilibrium vapour pressure is equal to the external pressure over the liquid, the liquid boils. The temperature at which this occurs is the boiling point. The energy that is required for boiling to occur is called the heat of vaporization.
- The strength of intermolecular forces governs the amount of energy needed to break bonds between the molecules of a liquid, so the boiling point, and the heat of vaporization both increase as the strength of intermolecular forces increase.

- For the general reaction:
  $aA + bB + \ldots \rightleftharpoons pP + qQ + \ldots$
  at constant temperature, the concentrations of reactants and products are related by the ratio:
  $$K_c = \frac{[P]^p[Q]^q\ldots}{[A]^a[B]^b\ldots}$$
  where K_c is the equilibrium constant for the reaction at a specified temperature.
- To calculate the value of the equilibrium constant, K_c, the concentrations of all reactants and products at equilibrium must be known, and are substituted into the equilibrium constant expression.
- As a closed system approaches equilibrium, the value of the concentration fraction $\frac{[P]^p[Q]^q\ldots}{[A]^a[B]^b\ldots}$ approaches the value of the equilibrium constant. If it is decreasing, then the reaction is progressing towards the left (making more reactants); if it is increasing, then the reaction is progressing towards the right (making more products).
- Calculations involving equilibrium constants can be undertaken using the table below.

Volume of reaction vessel (dm^3)	**Reactants**	**Products**
	Names of reactants	**Names of products**
Molar ratio in the equation		
Initial amount of substance, n_i (mol)		
Change (mol)		
Amount of substance at equilibrium, n_{eq} (mol)		
Concentration at equilibrium, $[\ ]_{eq}$ (mol dm^{-3})		

Chapter 6 Review questions

1 Describe the processes that occur when a sample of liquid is placed in an evacuated, sealed flask.

2 Explain why surface area has no effect on the equilibrium vapour pressure of a liquid.

3 Define the term *enthalpy of vaporization*.

4 Explain why the enthalpy of vaporization increases as the strength of intermolecular forces between molecules of the substance increases.

5 Explain the following differences in terms of intermolecular forces.

  a CH_3OH boils at 65°C while CH_3SH boils at 6°C.

  b Xe is a liquid at atmospheric pressure and 120 K, whereas Ar is a gas.

  c Propanone, CH_3COCH_3, boils at 56°C, whereas 2-methylpropane, $CH_3CH(CH_3)CH_3$ boils at –12°C.

6 From figure 6.1.3 (page 170) estimate the boiling point of propanone under an external pressure of 760 mmHg.

7 Identify the correct vapour pressure at 40°C for each of the following substances from the list below and explain your choices.

  Equilibrium vapour pressures: 134 mmHg, 279 mmHg, 55 mmHg

  a Ethanol, C_2H_5OH

  b Water, H_2O

  c Hexane, C_6H_{14}

8 Explain whether an egg could be hard boiled more quickly at sea level, 3 km above sea level or in a pressure cooker.

9 Calculate the equilibrium constant for the reaction shown below, given that the equilibrium concentrations of the species involved are $[H_2] = 0.23$ mol dm^{-3}, $[F_2] = 0.096$ mol dm^{-3} and $[HF] = 0.78$ mol dm^{-3}.

  $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

10 Two experiments are performed involving the oxidation of sulfur dioxide to sulfur trioxide according to the equation:

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

	$[SO_2]_{eq}$ (mol dm^{-3})	**$[O_2]_{eq}$ (mol dm^{-3})**	**$[SO_3]_{eq}$ (mol dm^{-3})**
Experiment 1	0.0831	0.161	0.855
Experiment 2	0.362	0.819	0.433

  a Calculate the equilibrium constant values for both experiments.

  b Determine which experiment was conducted at the higher temperature. Explain your answer.

11 A quantity of SO_2 in air is allowed to come to equilibrium in a container held at a temperature of 500°C:

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

Given the equilibrium concentrations of SO_2, O_2 and SO_3 are 0.282 mol dm^{-3}, 0.519 mol dm^{-3} and 0.303 mol dm^{-3} respectively, determine the value of the equilibrium constant, K_c, for the reaction at this temperature.

12 For the reaction shown in the equation below, calculate the concentration of I_2 at equilibrium, given that the equilibrium concentrations of H_2 and HI are 1.696×10^{-3} mol dm^{-3} and 1.181×10^{-2} mol dm^{-3} respectively.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_c = 410.5$ at 730 K

13 Ammonia and hydrogen react according to the equation:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad K_c = 0.650\ mol^{-2}\ dm^6$ at 200°C

- **a** Calculate the concentration of H_2 at equilibrium, given that $[N_2]_{eq} = 0.0381$ mol dm^{-3} and $[NH_3]_{eq} = 0.1096$ mol dm^{-3} at 200°C.
- **b** Would the value of the equilibrium constant increase, decrease or remain constant with an increase in temperature to 600°C, given that the forward reaction is exothermic?

14 A mixture of NO(g) and O_2(g) was allowed to come to equilibrium in a 1.4 dm^3 vessel. Analysis of the resulting contents showed 0.42 mol of NO, 0.28 mol of O_2 and 0.35 mol of NO_2. Calculate the equilibrium constant for the reaction:

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

15 A series of experiments were performed at a range of temperatures in which carbonyl bromide ($COBr_2$) was allowed to decompose to carbon monoxide and bromine according to the equation:

$COBr_2(g) \rightleftharpoons CO(g) + Br_2(g) \quad \Delta H > 0$

$K_c = 0.20$ mol dm^{-3} at 348 K

The equilibrium concentrations of the species recorded for each experiment are shown below:

	$[COBr_2]_{eq}$ (mol dm^{-3})	$[CO]_{eq}$ (mol dm^{-3})	$[Br_2]_{eq}$ (mol dm^{-3})
Experiment 1	0.0845	0.130	0.130
Experiment 2	0.639	0.0774	0.627
Experiment 3	0.0800	0.155	0.928
Experiment 4	0.120	0.273	0.0881

By calculating the equilibrium constant for each experiment, determine which of the experiments was conducted at:

- **a** 348 K
- **b** a temperature greater than 348 K
- **c** a temperature less than 348 K.

16 1.50 mol of carbon monoxide and 0.500 mol of chlorine gas are introduced into an evacuated 10.0 dm^3 vessel at 700 K. When the reaction reaches equilibrium, the concentration of phosgene ($COCl_2$) is 0.0485 mol dm^3. Calculate the equilibrium concentrations of CO and Cl_2 and so determine the equilibrium constant for the reaction at this temperature. The equation for the reaction is:

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

17 Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen gas, according to the equation:

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

$K_c = 810.5\ mol^{-1}\ dm^3$ at 500 K

Equal amounts of CO and H_2O are added to an evacuated vessel and allowed to come to equilibrium. Their concentrations are then both 0.0751 mol dm^{-3}. Calculate the concentrations of CO_2 and H_2 at equilibrium at this temperature.

18 The decomposition of hydrogen sulfide at 2000 K may be represented as

$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

1.40 mol of hydrogen sulfide was placed in a 2.0 dm^3 vessel and maintained at 2000 K until equilibrium reached. At equilibrium, 0.20 mol of gaseous sulfur was present.

- **a** Calculate the equilibrium constant for the reaction at 2000 K.
- **b** Another mixture of these gases also at 2000 K in a 2.0 dm^3 vessel was found to be made up of 0.6 mol H_2S(g), 0.45 mol H_2(g) and 0.3 mol S_2(g). Calculate the value of the concentration fraction for this mixture and hence determine in which direction the reaction must proceed in order to reach equilibrium.

Web Destinations www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter

Chapter 6 Test

Part A: Multiple-choice questions

1 Which combination is correct?

	$\Delta H_{\text{vaporization}}$	Boiling point	Intermolecular forces
A	large	high	strong
B	large	low	weak
C	small	low	strong
D	small	high	weak

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2 10.0 cm^3 of liquid bromine is placed in an empty 100 cm^3 bottle, which is then sealed and left to reach equilibrium at room temperature. What happens first?

A The rate of evaporation is greater than the rate of condensation.

B The rate of condensation is greater than the rate of evaporation.

C The rate of evaporation is equal to the rate of condensation.

D There is no evaporation or condensation.

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3 A 1.0 dm^3 reaction vessel initially contains 6.0 mol of **P** and 6.0 mol of **Q**. At equilibrium 4.0 mol of **R** is present. What is the value of K_c for the following reaction?

$P(g) + Q(g) \rightleftharpoons R(g) + S(g)$

A 0.11

B 0.25

C 0.44

D 4.00

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4 Which reaction uses a homogeneous catalyst?

A Iron in the Haber process

B Nickel in the conversion of alkenes to alkanes

C Acid in the formation of esters

D Manganese oxide in the decomposition of hydrogen peroxide

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5 A 1.0 dm^3 reaction vessel contains initially 1.0 mol of $NO_2(g)$ and 1.0 mol of $N_2O_4(g)$. At equilibrium, 0.75 mol of $N_2O_4(g)$ is present. What is the value of K_c?

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

A 0.33

B 0.50

C 2.0

D 3.0

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6 $N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 5.0 \times 10^{-3}$

In an equilibrium mixture of these two gases, $[N_2O_4] = 5.0 \times 10^{-1}$ mol dm^{-3}. What is the equilibrium concentration of NO_2 in mol dm^{-3}?

A 5.0×10^{-1}

B 5.0×10^{-2}

C 5.0×10^{-3}

D 2.5×10^{-4}

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7 The value of the equilibrium constant for the reaction

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

is 0.25 at 440°C. What would the value of the equilibrium constant be for the following reaction at the same temperature?

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

A 0.25

B 0.50

C 2.0

D 4.0

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8 A sealed container at room temperature is half full of water. The temperature of the container is increased and left for equilibrium to re-establish. Which statement is correct when the equilibrium is re-established at the higher temperature?

A The rate of vaporization is greater than the rate of condensation.

B The amount of water vapour is greater than the amount of liquid water.

C The amount of water vapour is greater than it is at the lower temperature.

D The rate of condensation is greater than the rate of vaporization.

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9 Iron(III) ions react with thiocyanate ions as follows.

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

What are the units of the equilibrium constant, K_c, for the reaction?

A mol dm^{-3}

B mol^2 dm^{-6}

C mol^{-1} dm^3

D mol^{-2} dm^6

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10 The expression for the equilibrium constant for a reaction is

$$K_c = \frac{[B][C]}{[A]^2}$$

At a certain temperature the values of [A], [B] and [C] are all 0.2 mol dm^{-3}. What happens to the value of K_c when all three values are doubled to 0.4 mol dm^{-3}?

A It is halved.

B It does not change.

C It doubles.

D It increases by a factor of four.

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(10 marks)

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 The equilibrium between nitrogen dioxide (dark brown) and dinitrogen tetroxide (colourless) is represented by the following equation.

$2NO_2(g) \rightleftharpoons N_2O_4(g)$ ΔH = negative, $K_c = 1$ at 328 K

Two moles of $NO_2(g)$ and two moles of $N_2O_4(g)$ were placed in an empty 1 dm^3 container and allowed to come to equilibrium at 328 K. Predict, with reference to the value of K_c, whether the equilibrium mixture would contain more or less than two moles of $NO_2(g)$.

(2 marks)

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2 In the gaseous state, methane and steam react to form hydrogen and carbon dioxide.

1.0 mol methane and 3.0 mol steam are placed in a container and after equilibrium is reached, 2.0 mol hydrogen gas are present. Calculate the amount of each reactant and product at equilibrium, and thus determine the value of K_c for the reaction.

(4 marks)

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3 The equation for another reaction used in industry is

$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$ $\Delta H^\ominus = -42$ kJ

a Under certain conditions of temperature and pressure, 2.0 mol of carbon monoxide and 3.2 mol of steam were left to reach equilibrium. At equilibrium,1.6 mol of both hydrogen and carbon dioxide were present.

Calculate the amounts of carbon monoxide and steam at equilibrium and the value of K_c.

(3 marks)

b Under the same conditions of temperature and pressure, 2.0 mol of carbon monoxide and 2.0 mol of steam were left to reach equilibrium

Calculate the amounts of each reactant and product at equilibrium.

(If you were unable to calculate a value for K_c in part **a**, use the value 9.0, although this is not the correct value.)

(2 marks)

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4 Consider the following reaction where colourless bromide ions react with colourless hydrogen peroxide to form a red-brown solution.

$2Br^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightleftharpoons Br_2(aq) + 2H_2O(l)$

ΔH = negative

State and explain the effect on the value of the equilibrium constant when the temperature of the reaction is increased.

(2 marks)

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Part C: Data-based question

a **i** Using the data below, state and explain the relationship between enthalpy of vaporization and intermolecular forces.

(3 marks)

Substance	Pentane	Propanoic acid
Standard enthalpy of vaporization $\Delta H^\ominus_v$ / kJ mol^{-1}	27	57

ii Draw a graph to show how the vapour pressure of pentane changes as it is heated from its melting point to its boiling point. Explain this change in terms of the kinetic theory.

(3 marks)

b **i** Consider the following reaction in the Contact process for the production of sulfuric acid.

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

1.50 mol of SO_2 and 2.00 mol of O_2 are placed in a 1.50 dm^3 flask and heated at 400°C until equilibrium is reached. The final equilibrium mixture contained 0.500 mol of SO_3. Calculate the equilibrium constant, K_c of the reaction at this temperature, include units in your answer.

(5 marks)

ii Using the following data, explain whether the above reaction is exothermic or endothermic

Temperature (K)	Equilibrium constant, K_c / dm^3 mol^{-1}
298	9.77×10^{25}
500	8.61×10^{11}
700	1.75×10^{6}

(2 marks)

IBO HL Paper 2 May 06 Q6e–g

Part D: Extended-response question

The equation for the decomposition of hydrogen iodide is

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g) \qquad \Delta H^\ominus = +52\ \text{kJ}$$

a Deduce the expression for K_c for the forward reaction.

(1 mark)

b The equilibrium formed during this reaction was investigated in two experiments carried out at different temperatures. The results are shown in the table below.

Experiment number	Initial concentration / mol dm^{-3}			Equilibrium concentration / mol dm^{-3}		
	[HI]	[H_2]	[I_2]	[HI]	[H_2]	[I_2]
1	0.06	0.00	0.00		0.01	
2	0.00	0.04	0.04	0.04		

i For each experiment, deduce the concentrations of the other species present at equilibrium. Calculate the values of K_c for the forward reaction for each experiment.

(6 marks)

ii Use the two calculated values of K_c to deduce which of the two experiments was carried out at the higher temperature, and explain your choice.

(If you were not able to calculate the values of K_c in part **i**, assume that the values are 0.1 for experiment 1 and 0.2 for experiment 2, although these are not the correct values.)

(2 marks)

IBO HL Paper 2 Nov 05 Q6b, c

Total marks: 45

7 ACIDS AND BASES

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 18: Acids and Bases.

By the end of this chapter, you should be able to:

- recognize that the pH scale is based on the equilibrium that exists between water and H_3O^+ and OH^- ions
- recall the definition of the ionic product constant of water: K_w
- recall that the value of K_w is temperature dependent
- recall the relationship between the equilibrium equation for the dissociation of an acid or base in aqueous solution and the acid or base dissociation constant, K_a or K_b
- distinguish between strong and weak acids and bases on the basis of their acid or base dissociation constant, or their pK_a or pK_b
- perform calculations of K_a and K_b values from relevant data
- deduce the pH of a weak acid or a weak base using values of K_a or K_b and other relevant data
- understand the role of buffers in maintaining a stable pH over a small range of values
- calculate the pH of a buffer system using relevant data
- deduce whether salts form acidic, alkaline or neutral aqueous solutions
- sketch graphs of pH against volume for titrations of combinations of strong acids, strong bases, weak acids and weak bases
- describe the important features of acid–base titration curves
- describe the nature of acid–base indicators and their action
- relate the pK_a of an indicator to its pH range
- identify an appropriate indicator for a titration.

IBO Assessment statements 18.1.1 to 18.5.3

Acids and bases are an important part of everyday life. We occasionally use strong acids such as hydrochloric acid for unusual tasks such as swimming pool maintenance and for cleaning mortar from bricks. A strong base such as sodium hydroxide can be used to clean blocked drains. It is so effective that it can be left to dissolve the oils and other debris that is blocking the drain without any extra work on our part. However, one of the more common roles that acids play in our lives is as a part of our foods. Despite the presence of hydrochloric acid in the stomach, we cannot consume strong acids safely, so the 'zing' in our foods is supplied by weak acids, such as phosphoric acid found in cola soft drinks, ethanoic acid in vinegar, citric acid in a wide variety of fruits (ranging from lemons to pineapples) and ascorbic acid (vitamin C) found in various fruits and as an additive to preserve foods. Sodium hydrogencarbonate (bicarbonate of soda) is a weak base and its reaction with the salt of a weak acid, such as cream of tartar (potassium hydrogen tartrate) in baking powder, provides the carbon dioxide that causes cakes to rise.

7.1 CALCULATIONS INVOLVING ACIDS AND BASES

Since Alessandro Volta invented the first battery in 1800, scientists have been interested in measuring the electrical conductivity of a wide range of materials. In order for a material to conduct electricity, it must contain charged particles and they must be free to move. The majority of metals are excellent conductors as their electrons are easily delocalized. Sea water readily conducts electricity due to the ionic salts dissolved in it. However, it was not until the development of very accurate measuring devices that scientists realized that even very pure water conducts electricity to a small extent. This was something of a surprise, as water is molecular and so very pure water should contain no charged particles—it should not be able to conduct electricity at all. It is now recognized that water undergoes *self-ionization* to a very small extent according to the equation:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Interactive Animation
Self-ionization of water

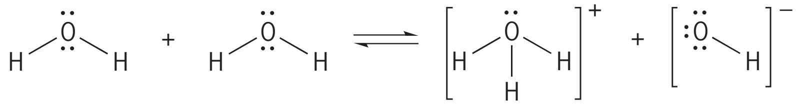

Figure 7.1.1 Water reacts with itself in an acid–base reaction called self-ionization.

The equilibrium constant expression for this equation is as follows:

$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_c \times [H_2O]^2 = [H_3O^+][OH^-]$$

As the concentration of water is very large and effectively a constant in aqueous solutions, the equilibrium expression can be transposed to give a new type of equilibrium constant called the **ionic product constant** or **ionization constant** of water (**K_w**), where:

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \text{ at } 25°\text{C}$$

18.1.1
State the expression for the ionic product constant of water (K_w). © IBO 2007

As can be seen from the magnitude of this equilibrium constant, the self-ionization of water occurs to only a very small extent at 25°C. Indeed, only approximately one molecule in 500 million actually undergoes ionization. Nevertheless, this is a critically important expression, as it forms the basis of the pH scale.

Calculations involving pH

You will recall from your acid–base studies in Standard Level Chemistry that pH is a measure of the acidity of a solution, and is defined as:

$$\text{pH} = -\log_{10}[H^+(aq)]$$

18.1.3
Solve problems involving $[H^+(aq)]$, $[OH^-(aq)]$, pH and pOH. © IBO 2007

This expression may also be written as

$$\text{pH} = -\log_{10}[H_3O^+]$$

The hydronium ion, H_3O^+, is formed in a Brønsted–Lowry acid–base reaction when a hydrogen ion, H^+, is donated to a water molecule, so $H_3O^+ = H^+(aq)$.

Interactive Animation
Acid–base strength

When $[H^+(aq)]$ needs to be calculated, this equation can be transposed to another useful form:

$$[H^+(aq)] = 10^{-\text{pH}} \text{ or } [H_3O^+] = 10^{-\text{pH}}$$

The ionic product constant, K_w, shows that the product of the concentrations of H_3O^+ and OH^- in aqueous solutions will always be 10^{-14} at 25°C, irrespective of how much acid or base is present. A neutral solution has, by definition, an equal concentration of acid and base ($[H_3O^+] = [OH^-]$).

The pH of this neutral solution can be calculated as follows:

$$K_w = [H_3O^+][OH^-] = 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

As $[H_3O^+] = [OH^-]$

$$[H_3O^+]^2 = 1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

$$[H_3O^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ \text{mol dm}^{-3}$$

By definition, $\text{pH} = -\log_{10}[H_3O^+]$

$$\text{pH} = -\log_{10}(1.0 \times 10^{-7})$$

$$\text{pH} = 7$$

A solution with $\text{pH} < 7$ is known as an acidic solution.

Since $[H_3O^+] = 10^{-\text{pH}}$,

it follows that if the $\text{pH} < 7$, then $[H_3O^+] > 1.0 \times 10^{-7}\ \text{mol dm}^{-3}$ at 25°C.

Similarly, a solution with $\text{pH} > 7$ is known as an alkaline (basic) solution.

Since $[H_3O^+] = 10^{-pH}$

it follows that if the pH > 7, then $[H_3O^+] < 1.0 \times 10^{-7}$ mol dm^{-3} at 25°C.

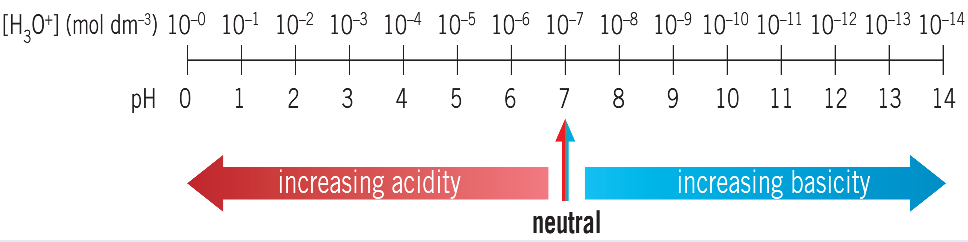

Figure 7.1.2 The pH scale at 25°C.

If the concentration of a basic solution is given and the pH is required, the expression for K_w can be rearranged to give a value of $[H_3O^+]$ and then pH can be calculated as usual.

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

Worked example 1

Determine the pH of solutions of the following concentrations.

a $[HNO_3] = 3.74 \times 10^{-5}$ mol dm^{-3}

b $[H_2SO_4] = 2.50 \times 10^{-3}$ mol dm^{-3}

c $[KOH] = 7.75 \times 10^{-2}$ mol dm^{-3}

d $[Ba(OH)_2] = 0.00050$ mol dm^{-3}

Solution

a Note that nitric acid is a strong monoprotic acid and so, effectively, all of the HNO_3 molecules will dissociate in solution to produce hydronium ions, H_3O^+.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

This means that the concentration of H_3O^+ ions in solution will be equal to the concentration of HNO_3:

$$[HNO_3] = [H_3O^+] = 3.74 \times 10^{-5} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(3.74 \times 10^{-5}) = 4.43$$

b Sulfuric acid is a strong diprotic acid. In calculations we assume that all of the H_2SO_4 molecules dissociate fully in solution:

$$H_2SO_4(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$$

So $[H_3O^+] = 2[H_2SO_4]$

$$[H_3O^+] = 2 \times (2.50 \times 10^{-3}) = 5.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(5.00 \times 10^{-3}) = 2.30$$

c Potassium hydroxide is a soluble hydroxide and dissociates completely in solution, according to the equation:

$$KOH(aq) \xrightarrow{\text{water}} K^+(aq) + OH^-(aq)$$

$$[KOH] = [OH^-] = 7.75 \times 10^{-2} \text{ mol dm}^{-3}$$

However, $[H_3O^+]$ needs to be calculated before pH can be found:

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$

$[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{7.75 \times 10^{-2}} = 1.29 \times 10^{-13}\ mol\ dm^{-3}$

$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.29 \times 10^{-13}) = 12.9$

d Barium hydroxide is also a soluble hydroxide and dissociates completely in solution, according to the equation:

$$Ba(OH)_2(aq) \xrightarrow{water} Ba^{2+}(aq) + 2OH^-(aq)$$

This means that $[OH^-] = 2[Ba(OH)_2]$

$[Ba(OH)_2] = 0.00050\ mol\ dm^{-3} = 5.0 \times 10^{-4}\ mol\ dm^{-3}$

$[OH^-] = 2 \times 5.0 \times 10^{-4}\ mol\ dm^{-3} = 1.0 \times 10^{-3}\ mol\ dm^{-3}$

$K_w = [H_3O^+][OH^-] = 10^{-14}\ mol^2\ dm^{-6}$

$[H_3O^+] = \dfrac{1.00 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\ mol\ dm^{-3}$

$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.0 \times 10^{-11}) = 11$

* * *

Up to this point we have only come across one instance in which $-\log_{10}$ of a value is taken: $pH = -\log_{10}[H^+]$ (also written as $pH = -\log_{10}[H_3O^+]$); however, this use of the letter p is actually a form of standard notation. The letter p in front of a symbol for concentration indicates that $-\log_{10}$ of that concentration should be calculated.

For example:

$pH = -\log_{10}[H^+]$
$pOH = -\log_{10}[OH^-]$
$pK_w = -\log_{10}K_w$

We will encounter further examples of this notation later in this chapter.

The expressions for **pOH** and pK_w are useful when determining the pH of an alkaline solution.

If $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}\ mol^2\ dm^{-6}$

then $-\log_{10} K_w = -\log_{10}[H_3O^+] + -\log_{10}[OH^-] = -\log_{10}1.0 \times 10^{-14}$

and

$pK_w = pH + pOH = 14$

If a value for pOH is calculated, then $pH = 14 - pOH$

Worked example 2

Determine the pH of solutions of the following concentrations.

a $[NaOH] = 3.34 \times 10^{-5}$ mol dm^{-3}

b $[Mg(OH)_2] = 2.50 \times 10^{-4}$ mol dm^{-3}

Solution

a $NaOH(s) \xrightarrow{\text{water}} Na^+(aq) + OH^-(aq)$

$[NaOH] = [OH^-] = 3.34 \times 10^{-5}$ mol dm^{-3}

$$\begin{aligned} pOH &= -\log_{10}[OH^-] \\ &= -\log_{10}(3.34 \times 10^{-5}) = 4.48 \\ pH &= 14 - pOH \\ &= 14 - 4.48 = 9.52 \end{aligned}$$

b $Mg(OH)_2(s) \xrightarrow{\text{water}} Mg^{2+}(aq) + 2OH^-(aq)$

so $[OH^-] = 2[Mg(OH)_2]$

$[Mg(OH)_2] = 2.50 \times 10^{-4}$ mol dm^{-3}

$[OH^-] = 2 \times 2.50 \times 10^{-4}$ mol dm^{-3} $= 5.00 \times 10^{-4}$ mol dm^{-3}

$$\begin{aligned} pOH &= -\log_{10}[OH^-] \\ &= -\log_{10}(5.00 \times 10^{-4}) = 3.30 \\ pH &= 14 - pOH \\ &= 14 - 3.30 = 10.7 \end{aligned}$$

Worked example 3

25.0 cm^3 of 8.00 mol dm^3 nitric acid is diluted to 200 cm^3 with distilled water. Calculate the pH of the resultant solution.

Solution

As the nitric acid solution has been diluted, we can use $c_1V_1 = c_2V_2$.

$c_1 = 8.00$ mol dm^{-3}, $V_1 = 25.0$ cm^3, $c_2 = ?$, $V_2 = 25.0$ cm^3 + 175 cm^3 = 200 cm^3

Note that units of volume do not need to be converted to dm^3 because they will be cancelled out during the calculation. The only requirement is that the units are the same for V_1 and V_2.

$$\begin{aligned} c_1V_1 &= c_2V_2 \\ 8.00 \times 25.0 &= c_2 \times 200 \\ c_2 &= \frac{8.00 \times 25.0}{200} \\ c_2 &= 1.00 \text{ mol dm}^{-3} \end{aligned}$$

$[HNO_3] = [H_3O^+] = 1.00$ mol dm^{-3}

$$\begin{aligned} pH &= -\log_{10}[H_3O^+] \\ &= -\log_{10}1.00 \\ pH &= 0.00 \end{aligned}$$

Worked example 4

80.0 cm^3 of 2.00 mol dm^{-3} nitric acid is added to 120 cm^3 of 0.150 mol dm^3 hydrochloric acid. Calculate the pH of the resultant solution.

Solution

In this case, two acids have been mixed. They will not react with each other, but each will contribute hydronium ions to the total solution. To solve the problem, the total amount in mol of H_3O^+ contributed by the two acids must be divided by the total volume of solution to determine the overall concentration of H_3O^+. The pH can then be determined in the usual manner.

$$n(H_3O^+) = n(HNO_3) + n(HCl)$$
$$n(H_3O^+) = 2.00 \times 0.0800 + 0.150 \times 0.120 = 0.178 \text{ mol}$$
$$V_T = 80.0 \text{ cm}^3 + 120 \text{ cm}^3 = 200 \text{ cm}^3 = 0.200 \text{ dm}^3$$
$$[H_3O^+] = \frac{n}{V} = \frac{0.178}{0.200} = 0.890 \text{ mol dm}^{-3}$$
$$\text{As pH} = -\log_{10}[H_3O^+] = -\log_{10}(0.890)$$
$$\text{pH} = 0.0506$$

CHEM COMPLEMENT

Aqua regia and the Nobel Prize medals

Aqua regia is a mixture of one part concentrated nitric acid to three parts concentrated hydrochloric acid. Its discovery has been credited to the Islamic alchemist Abu Musa Jābir Ibn Hayyān. It has the rare ability to dissolve gold by using the competing equilibria between the two equilibria:

$$Au(s) \rightleftharpoons Au^{3+}(aq) + 3e^-$$
$$Au^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons AuCl_4^-(aq)$$

During World War II this ability was apparently put to a vital use in Denmark by the Hungarian chemist George de Hevesy.

Two German Jewish physicists, Max von Laue and James Franck, had sought refuge in Copenhagen at the Institute of Theoretical Physics with Professor Niels Bohr. They brought their precious gold Nobel Prize medals with them from Germany—a serious offence in Hitler's Germany. When Denmark was occupied in 1940, the medals, which were engraved with the names of their owners, needed to be hidden, since their discovery would have had dire consequences for von Laue and Franck. George de Hevesy found the ultimate way to hide the golden medals—he dissolved them in aqua regia and stored the solution with a variety of other solutions on the laboratory shelves. The bottles were not taken by the occupying forces and after the war the gold was recovered and returned to the Nobel Foundation. New medals were presented to von Laue and Franck in the early 1950s.

Figure 7.1.3 The Nobel Prize medals that were dissolved by George de Hevesy in order to save them were made of 23-karat gold, weighed approximately 200 g and had a diameter of 66 mm.

Worked example 5

180 cm^3 of 1.25 mol dm^{-3} hydrochloric acid is reacted with 240 cm^3 of 0.886 mol dm^{-3} sodium hydroxide solution. Calculate the pH of the resultant solution.

Solution

In this case, an acid and a base have been reacted. If the number of mole of acid and base are the same, the solution will be neutral. If, however, one of the reactants is in excess, the remaining substance will determine the overall pH of the resulting solution.

The equation representing this neutralization reaction is:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
$$n(H_3O^+) = n(HCl) = cV = 1.25 \times 0.180 = 0.225 \text{ mol}$$
$$n(OH^-) = n(NaOH) = cV = 0.886 \times 0.240 = 0.213 \text{ mol}$$

There is a slight excess of HCl, so:

$$n(H_3O^+) \text{ in excess} = 0.225 - 0.213 = 0.0124 \text{ mol}$$
$$V_T = 180 \text{ cm}^3 + 240 \text{ cm}^3 = 420 \text{ cm}^3 = 0.420 \text{ dm}^3$$
$$[H_3O^+] = \frac{n}{V} = \frac{0.0124}{0.420} = 0.0295 \text{ mol dm}^{-3}$$
$$pH = -\log_{10}[H_3O^+] = -\log_{10}(0.0295)$$
$$pH = 1.53$$

THEORY OF KNOWLEDGE

The origins and meanings of the chemical terms we use come from many different languages. Aqua regia is Latin for 'royal water', so named because it could dissolve gold, a noble or unreactive metal.

- The word *alkali* has Arabic roots. The term originally meant 'roasting', because the first alkaline substances were obtained by roasting ashes then treating them with water and slaked lime (calcium hydroxide). Can you think of any terms we use in acid–base chemistry that have origins in a language other than English? Check out the origin of the word 'acid'.
- Problems with meaning can arise when words are translated between languages. Find a chemical term in a language that is similar to the term we use in English. Compare their meanings.
- The meanings of words change depending on the context. Find out how the words *noble* and *alkali* are used in non-scientific contexts.

The temperature dependence of K_w

The ionic product constant of water, K_w, is based on chemical equilibrium, and so is temperature-dependent:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = +57 \text{ kJ mol}^{-1}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25°C$$

As this is an endothermic reaction in the forward direction, an increase in temperature above 25°C will cause the reaction to proceed in the forward direction, thus increasing the concentrations of both H_3O^+ and OH^- ions. The equilibrium constant (K_w) will also increase with an increase in temperature. If the temperature is decreased to below 25°C, the reaction will proceed to the left and the concentrations of H_3O^+ and HO^- ions will decrease.

As pH is defined in terms of the concentration of H_3O^+ ions, when an increase in temperature results in a higher concentration of H_3O^+ it also results in a lower pH for pure water. In the same way, when a decrease in temperature forces the reaction backwards, the concentration of H_3O^+ decreases and the pH increases.

Does this mean that if we heat or cool water it will become either more or less acidic? It is important to note that the concentrations of both H_3O^+ and OH^- will increase or decrease to precisely the same extent with a change in temperature, as can be seen from the stoichiometric 1 : 1 ratio in the equation. Thus, even though both the concentration of H_3O^+ and the pH change with temperature, the water will remain neutral.

AS 18.1.2
Deduce [H^+(aq)] and [OH^-(aq)] for water at different temperatures given K_w values. © IBO 2007

It is important to make a clear distinction between 'neutral' and pH 7. Pure water is always neutral, but it only has a pH of precisely 7 at 25°C. Unless the question states otherwise, it is reasonable, when calculating pH, to assume that the temperature is 25°C.

WORKSHEET 7.1
pH and K_w

TABLE 7.1.1 K_w AND pH VALUES FOR PURE WATER

Temperature (°C)	K_w (mol^2 dm^{-6})	pH
0	1.14×10^{-15}	7.47
10	2.92×10^{-15}	7.27
20	6.81×10^{-15}	7.08
25	1.00×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.5×10^{-14}	6.26
100	5.5×10^{-13}	5.26

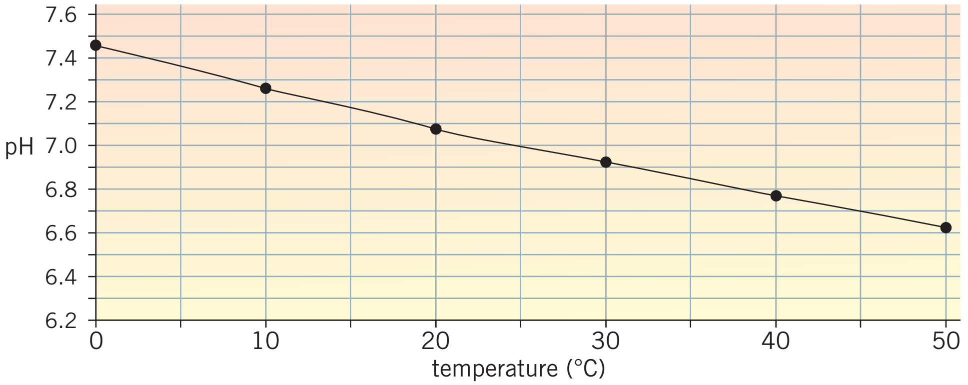

Figure 7.1.4 The pH of pure water varies with temperature.

Worked example 6

Deduce $[H_3O^+]$ and $[OH^-]$ for a sample of pure water at 40°C.

Solution

From table 7.1.1, at 40°C $K_w = 2.92 \times 10^{-14}$ mol^2 dm^{-6}

$$[H_3O^+][OH^-] = 2.92 \times 10^{-14}$$

In pure water we would expect that $[H_3O^+] = [OH^-]$

$$[H_3O^+]^2 = 2.92 \times 10^{-14}$$

$$[H_3O^+] = \sqrt{2.29 \times 10^{-14}}$$

$$= 1.71 \times 10^{-7} \text{ mol dm}^{-3}$$

And $[OH^-] = 1.71 \times 10^{-7}$ mol dm^{-3}

Section 7.1 Exercises

1 Assuming complete ionization, calculate the pH of each of the following solutions at 298 K.

- **a** $[HNO_3] = 1.0 \times 10^{-3}$ mol dm^{-3}
- **b** $[HCl] = 0.00624$ mol dm^{-3}
- **c** $[H_2SO_4] = 2.34 \times 10^{-5}$ mol dm^{-3}
- **d** $[NaOH] = 6.5 \times 10^{-2}$ mol dm^{-3}
- **e** $[LiOH] = 3.5 \times 10^{-3}$ mol dm^{-3}
- **f** $[Ba(OH)_2] = 5.0 \times 10^{-4}$ mol dm^{-3}

2 Assuming complete ionization, calculate the pOH of each of the following solutions at 298 K.

- **a** $[NaOH] = 1.5 \times 10^{-6}$ mol dm^{-3}
- **b** $[HCl] = 0.00245$ mol dm^{-3}
- **c** $[H_2SO_4] = 9.05 \times 10^{-5}$ mol dm^{-3}
- **d** $[Ca(OH)_2] = 0.15$ mol dm^{-3}

3 Calculate $[H^+(aq)]$ of each of the following solutions at 298 K.

- **a** HCl(aq) with pH = 2.5
- **b** HNO_3(aq) with pH = 1.75
- **c** KOH(aq) with pOH = 2.2
- **d** NaOH(aq) with pOH = 3.5

4 Calculate the pH of the solution formed by bubbling 0.225 mol of hydrogen chloride gas (HCl) through 1.50 dm^3 of water.

5 **a** 85.0 cm^3 of 1.35 mol dm^{-3} hydrochloric acid is diluted to 600 cm^3 with distilled water. What is the pH of the resultant solution?

b Calculate the pH of the solution that would result when 265 cm^3 of water is added to 15.0 cm^3 of 8.00 mol dm^{-3} nitric acid.

6 3.73 g of potassium hydroxide pellets are carefully dissolved in 250 cm^3 of water. Calculate the pH of the resultant solution.

7 Determine the pH of the solution that results from the addition of 85.0 cm^3 of 0.117 mol dm^{-3} hydrochloric acid to 135 cm^3 of 0.0955 mol dm^{-3} lithium hydroxide.

8 340.0 cm^3 of 0.00334 mol dm^{-3} sodium hydroxide is mixed with 265 cm^3 of 8.45×10^{-4} mol dm^{-3} potassium hydroxide solution. Calculate the pH of the resultant solution.

9 A sample of water was heated over a Bunsen burner until its temperature was 60°C. Describe how the pH of the water will change as the water cooled to 25°C.

10 **a** From figure 7.1.4, determine:

- **i** the $[H_3O^+]$ in pure water at 20°C
- **ii** the $[OH^-]$ in pure water at 35°C
- **iii** K_w for pure water at 45°C.

b Is the self-ionization of water endothermic or exothermic? Deduce your answer by considering figure 7.1.4, and explain your reasoning.

7.2 ACID AND BASE DISSOCIATION CONSTANTS

When an acid reacts with water, it produces hydronium, H_3O^+, ions as a result of the donation of a hydrogen ion to the water molecule. For any acid, HA, we can write an equation to represent this reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

AS 18.1.4
State the equation for the reaction of any weak acid or weak base with water, and hence deduce the expressions for K_a and K_b. © IBO 2007

The species A^- is the conjugate base of the acid HA. For a strong acid, the position of equilibrium will be far to the right and the majority of HA molecules will lose their H^+ ions, forming H_3O^+.

A large equilibrium constant will accompany such a reaction. Conversely, for a weak acid, the position of equilibrium will be towards the left, there will be few products, therefore a low $[H_3O^+]$ and the equilibrium constant will be small.

The equilibrium constant expression for the general reaction of an acid with water is:

$$K_c = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

Equilibrium constant expressions can be written for a variety of specific classes of reactions. We have already seen one specialized example of such an equilibrium constant in the ionic product constant of water, K_w.

Two other important examples of these more specialized equilibrium constant expressions are the **acid** and **base dissociation constants, K_a** and **K_b**.

In the equilibrium constant expression above, the concentration of water is effectively a constant and so it can be written as:

$$K_c \times [H_2O] = \frac{[A^-][H_3O^+]}{[HA]}$$

When $[H_2O]$ is incorporated in the equilibrium constant, it becomes the acid dissociation constant, K_a.

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

When a base reacts with water, it accepts an H^+ ion from the water molecule. For any base, B, we can write an equation to represent this reaction:

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The species HB^+ is the conjugate acid of the base B. The position of equilibrium for a strong base will lie far to the right, and for a weak base, to the left. A strong base will have a large equilibrium constant and a weak base will have a small equilibrium constant.

The equilibrium constant expression for the general reaction of a base with water is:

$$K_c = \frac{[HB^+][OH^-]}{[B][H_2O]}$$

This can be written as:

$$K_c \times [H_2O] = \frac{[HB^+][OH^-]}{[B]}$$

When $[H_2O]$ is incorporated in the equilibrium constant, it becomes the base dissociation constant, K_b.

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Worked example 1

Ethanoic acid (CH_3COOH) is the principal acidic constituent of vinegar. Write an expression for the acidity constant of ethanoic acid.

Solution

The relevant equation is:

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

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

AS **18.1.6**
Identify the relative strengths of acids and bases using values of K_a, K_b, pK_a and pK_b.
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Acid dissociation constants are useful indicators of the relative strengths of acids—the larger the value, the stronger is the acid. For example, hydrochloric acid has a K_a value of 10^7 mol dm^{-3}, whereas for ethanoic acid K_a is only 1.74×10^{-5} mol dm^{-3}.

Base dissociation constants indicate the strength of a base. Ammonia is a weak base and has a K_b of 1.78×10^{-5} mol dm^{-3}. The organic base ethylamine, $C_2H_5NH_2$, is a stronger base than ammonia, with a K_b of 5.37×10^{-4} mol dm^{-3}.

PRAC 7.1
Determination of the K_a of a weak acid

Acid and base dissociation con stants have been determined for a wide range of substances and some of their values are listed in tables 7.2.1 and 7.2.2 as pK_a and pK_b values. You will recall that 'p' in front of a term indicates that $-\log_{10}$ should be calculated.

So

$$\mathbf{p}K_a = -\log_{10} K_a$$

$$\mathbf{p}K_b = -\log_{10} K_b$$

Just as a small K_a indicates a weak acid and a small K_b indicates a weak base, a large pK_a indicates a weak acid and a large pK_b indicates a weak base.

The larger the pK_a the weaker the acid, the larger the pK_b, the weaker the base.

TABLE 7.2.1 K_a AND pK_a VALUES AT 25°C FOR SOME COMMON WEAK ACIDS
(More values can be found in Appendix 5 and in table 15 of the IB Data booklet. © IBO 2007)

Name	Formula	K_a value (mol dm^{-3})	pK_a
Methanoic acid	$HCOOH$	1.78×10^{-4}	3.75
Ethanoic acid	CH_3COOH	1.74×10^{-5}	4.76
Propanoic acid	CH_3CH_2COOH	1.35×10^{-5}	4.87
Butanoic acid	$CH_3CH_2CH_2COOH$	1.51×10^{-5}	4.82
Boric acid	H_3BO_3	5.75×10^{-10}	9.24
Hypochlorous acid	$HOCl$	2.88×10^{-8}	7.54
Hydrocyanic acid	HCN	6.03×10^{-10}	9.22
Hydrofluoric acid	HF	6.76×10^{-4}	3.17
Nitrous acid	HNO_2	7.24×10^{-4}	3.14

TABLE 7.2.2 K_b AND pK_b VALUES AT 25°C FOR SOME COMMON WEAK BASES

(More values can be found in table 15 of the IB Data booklet. © IBO 2007)

Name	Formula	K_b value (mol dm^{-3})	pK_b
Ammonia	NH_3	1.78×10^{-5}	4.75
Methylamine	CH_3NH_2	4.37×10^{-4}	3.36
Ethylamine	$CH_3CH_2NH_2$	5.37×10^{-4}	3.27
Dimethylamine	$(CH_3)_2NH$	5.25×10^{-4}	3.28
Trimethylamine	$(CH_3)_3N$	6.31×10^{-5}	4.20
Phenylamine	$C_6H_5NH_2$	4.17×10^{-10}	9.38
Pyridine	C_5H_5N	1.70×10^{-9}	8.77
Hydrazine	H_2NNH_2	1.29×10^{-6}	5.89

Worked example 2

Compare the acidity of boric acid, methanoic acid and propanoic acid.

Solution

From table 7.2.1 pK_a values for these substances are

boric acid 9.24 methanoic acid 3.75 propanoic acid 4.87

The larger the pK_a value, the weaker the acid, so of these three substances, boric acid is the weakest acid and methanoic acid is the strongest acid. Propanoic acid falls between these two in terms of acid strength.

The order of acidity is

boric acid < propanoic acid < methanoic acid

Worked example 3

If benzoic acid has a pK_a of 4.20, calculate its K_a.

Solution

Since $pK_a = -\log_{10} K_a$

$$\begin{aligned} \text{Then } K_a &= 10^{-pK_a} \\ &= 10^{-4.2} \\ &= 6.3 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

Problems involving solutions of weak acids and bases

Earlier we saw that the reaction of a base with water could be represented as

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

and that of an acid with water could be represented as

$$\underset{\text{acid}}{HA(aq)} + H_2O(l) \rightleftharpoons \underset{\text{conjugate base}}{A^-(aq)} + H_3O^+(aq)$$

AS **18.1.5**
Solve problems involving solutions of weak acids and bases using the expressions:
$K_a \times K_b = K_w$
$pK_a + pK_b = pK_w$
$pH + pOH = pK_w$.
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The acid dissociation constant, K_a, for this reaction is:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

If the conjugate base of an acid reacts with water, this equation is written as

$$\mathbf{A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)}$$

and the base dissociation constant, K_b, for this reaction is:

$$K_b = \frac{[HA][OH]}{[A^-]}$$

An important relationship exists between a weak acid HA represented by K_a and its conjugate base A^- represented by K_b:

$$\begin{aligned} K_a \times K_b &= \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} \\ &= [H_3O^+][OH^-] \\ &= K_w = 1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6} \end{aligned}$$

For any weak acid and its conjugate base: $K_a \times K_b = K_w$

If $-\log_{10}$ of each of these quantities is calculated, it follows that:

$$-\log_{10} K_a + -\log_{10} K_b = -\log_{10} K_w$$

$$\mathbf{pK_a + pK_b = pK_w}$$

This relates the pK_a of an acid and the pK_b of its conjugate base to the ionic product constant of water.

Acid and base dissociation constants are useful in performing calculations involving pH for weak acids and bases.

In the previous examples of the calculation of pH for strong acids, we could assume that the reactions were effectively complete, so that the concentration of H_3O^+ was the same as the initial acid concentration.

For example, the pH of a 0.10 mol dm^{-3} solution of hydrochloric acid is 1. The relevant hydrolysis reaction is:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq) \qquad K_a = 1 \times 10^7$$

The reaction proceeds so far to the right that it is valid to assume that:

$$[HCl] = [H_3O^+] = 0.10\ \text{mol dm}^{-3}$$

$$\begin{aligned} \text{As pH} &= -\log_{10} [H_3O^+] \\ \text{pH} &= -\log_{10} (0.10) \\ \text{pH} &= 1.0 \end{aligned}$$

Such an assumption is not valid for a weak acid such as ethanoic acid. The reaction proceeds to only a relatively small extent, as shown by the very small equilibrium constant:

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

$$K_a = 1.74 \times 10^{-5}\ \text{mol dm}^{-3}$$

A 0.10 mol dm^{-3} solution of ethanoic acid does not have a pH of 1.0, but rather 2.9. Only a small proportion of the CH_3COOH molecules are ionized to CH_3COO^-; the remainder are left unreacted. The pH of a weak acid can be measured with a pH meter or pH paper; however, it can also be determined mathematically.

WORKSHEET 7.2
Acid equilibria

Figure 7.2.1 The pH of a dilute solution of ethanoic acid can be determined experimentally using a pH meter.

Worked example 4

Calculate the pH of a 1.00×10^{-3} mol dm^{-3} solution of ethanoic acid, given that $K_a = 1.74 \times 10^{-5}$ mol dm^{-3}.

Solution

The equation for the hydrolysis of ethanoic acid is:

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

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$$

From the equation, $[CH_3COO^-] = [H_3O^+]$ at equilibrium, and so:

$$K_a = \frac{[H_3O^+]^2}{[CH_3COOH]} = 1.74 \times 10^{-5}$$

We also know from the equation that:

$$[CH_3COOH]_i = [CH_3COOH]_{eq} + [CH_3COO^-]_{eq} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$$

However, as CH_3COOH is a weak acid, it will ionize to only a small extent and so $[CH_3COO^-]_{eq}$ will be very small. As a consequence, the concentration of ethanoic acid will remain virtually constant at 1.00×10^{-3} mol dm^{-3}.

For our calculation, we make the assumption that:

$$[CH_3COOH]_i \cong [CH_3COOH]_{eq} = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$$

From earlier calculations:

$$\frac{[H_3O^+]^2}{[CH_3COOH]} = 1.74 \times 10^{-5}$$

$$\frac{[H_3O^+]^2}{1.00 \times 10^{-3}} = 1.74 \times 10^{-5}$$

$$[H_3O^+]^2 = 1.74 \times 10^{-8}$$

$$[H_3O^+] = \sqrt{1.74 \times 10^{-8}}$$

$$[H_3O^+] = 1.32 \times 10^{-4} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.32 \times 10^{-4}) = 3.88$$

Note that without the assumption that $[CH_3COOH]$ at equilibrium is equal to $[CH_3COOH]$ initially, calculations such as these could not be performed. In addition, we are also assuming that the concentration of H_3O^+ due to the self-ionization of water is negligible and so will not affect the calculated pH value.

It is important to recognize that, as they are equilibrium constants, acidity constants do not vary with the concentration of the acid solution, but only change with temperature. For the purposes of the calculations, the temperature will be assumed to be 25°C in all cases.

Figure 7.2.2 Hypochlorous acid is an active ingredient in household bleach and pool chlorine.

Worked example 5

Hypochlorous acid (HOCl) is widely used as a germicide in bleaches and swimming pools, as it kills bacteria effectively. A 0.250 mol dm^{-3} solution of hypochlorous acid has a measured pH of 4.07. Use this information to determine the acid dissociation constant, written as a pK_a value, of hypochlorous acid.

Solution

The equation for the hydrolysis of hypochlorous acid is:

$$HOCl(aq) + H_2O(l) \rightleftharpoons OCl^-(aq) + H_3O^+(aq)$$

$$pH = 4.07$$
$$[H_3O^+] = 10^{-4.07} = 8.51 \times 10^{-5} \text{ mol dm}^{-3}$$

From the equation, $[H_3O^+]_{eq} = [OCl^-]_{eq} = 8.51 \times 10^{-5}$ mol dm^{-3}

and $[HOCl]_i \cong [HOCl]_{eq} = 0.250$ mol dm^{-3} for a weak acid.

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]}$$

$$K_a = \frac{(8.51 \times 10^{-5})^2}{0.250}$$

$$K_a = 2.90 \times 10^{-8} \text{ mol dm}^{-3}$$

$$pK_a = -\log_{10}(2.90 \times 10^{-8}) = 7.54$$

Section 7.2 exercises

1 For each of the following monoprotic acids:

- **i** Write the equation for the dissociation of the acid in water.
- **ii** Write the expression for the acid dissociation constant, K_a.

a Methanoic acid (HCOOH)

b Hypobromous acid (HOBr)

c Hydrogen sulfate ion (HSO_4^-)

2 For each of the following bases:

- **i** Write the equation for the dissociation of the base in water.
- **ii** Write the expression for the base dissociation constant, K_b

a Ethylamine ($CH_3CH_2NH_2$)

b Trimethylamine ($(CH_3)_3N$)

c Phenylamine ($C_6H_5NH_2$)

3 Copy and complete the table below.

Monoprotic acid	**K_a (mol dm^{-3})**	**pK_a**
Phenylethanoic acid	4.90×10^{-5}	
Boric acid		9.24
Bromoethanoic acid		2.90
Pentanoic acid	1.38×10^{-5}	

4 Copy and complete the table below.

Base	**K_b (mol dm^{-3})**	**pK_b**
Ammonia		4.75
Methylamine	4.37×10^{-4}	
Diethylamine		3.07
Phenylamine	4.17×10^{-10}	

5 Hydrocyanic acid (HCN) is a weak monoprotic acid with a K_a value of 6.0×10^{-10} mol dm^{-3}. Calculate the pH of a 0.50 mol dm^{-3} solution of hydrocyanic acid.

6 Determine the pH of:

a a solution with an ethanoic acid concentration of 0.524 mol dm^{-3} (pK_a ethanoic acid = 4.76)

b a solution with a pentanoic acid concentration of 8.25×10^{-3} mol dm^{-3} (pK_a pentanoic acid = 4.86)

c 200 cm^3 of solution in which 8.05 g of methanoic acid has been dissolved (pK_a methanoic acid = 3.75)

7 For each of the following solution at 25°C, determine:

i the pOH **ii** the pH

a A solution with an ammonia concentration of 0.123 mol dm^{-3} (pK_b ammonia = 4.75)

b A solution with a methylamine concentration of 4.25×10^{-4} mol dm^{-3} (pK_b methylamine = 3.36)

8 For each of the following weak acids deduce:

i the formula of the conjugate base

ii the value of pK_b for the conjugate base at 298 K

a Methanoic acid, HCOOH (pK_a = 3.75)

b Propanoic acid, C_2H_5COOH (pK_a = 4.87)

c Chloroethanoic acid, $CH_2ClCOOH$ (pK_a = 2.86)

9 Order the acids listed in question **8** from strongest acid to weakest acid.

10 The ammonium ion is the weak conjugate acid of the base ammonia.

a Determine the equation for the dissociation of the ammonium ion in water.

b Given that a 0.040 mol dm^{-3} solution of ammonium nitrate has a pH of 5.32, calculate the acid ionization constant for the ammonium ion.

7.3 BUFFER SOLUTIONS

AS 18.2.1 Describe the composition of a buffer solution and explain its action. © IBO 2007

A constant pH is often required in living systems in which a small change in the pH may have dramatic and even undesirable results. For example, proteins may become denatured and the solubility of gases may decrease. Blood is a particularly sensitive system whose pH must stay at 7.4. The pH of a system can be stabilized by creating a mixture of solutes known as a **buffer solution**. A buffer solution resists changes in pH when a small amount of an acid or a base is added. Natural buffers occur in living systems and can be imitated in the laboratory.

An **acidic buffer solution** may be made up of a weak acid and the salt of its conjugate base (e.g. ethanoic acid, CH_3COOH, and sodium ethanoate, CH_3COONa). The equilibrium of the weak acid is:

$$\underbrace{HA(aq)}_{\text{weak acid}} + H_2O(l) \rightleftharpoons \underbrace{A^-(aq)}_{\text{conjugate base}} + H_3O^+(aq)$$

This equilibrium lies significantly to the left, with a larger proportion of reactants (weak acid) than products.

Interactive CW Animation
Buffer solution

The salt may be represented as MA, where M^+ is a positive ion from a strong base and A^- is the conjugate base of the weak acid. The salt could be formed by the reaction between a strong base such as sodium hydroxide, NaOH, and a weak acid such as ethanoic acid, CH_3COOH.

$$\underbrace{MOH(aq)}_{\text{strong base}} + \underbrace{HA(aq)}_{\text{weak acid}} \rightarrow H_2O(l) + \underbrace{MA(aq)}_{\text{salt}}$$

The salt then dissociates completely:

$$MA(aq) \rightarrow M^+(aq) + A^-(aq)$$

CHEM COMPLEMENT

Buffering our blood

Respiration occurs in all the cells of the body, using oxygen and producing carbon dioxide as a waste product. When carbon dioxide dissolves it forms carbonic acid, which causes a drop in pH.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

The equilibrium involved in the binding of oxygen to hemeglobin (Hb) for transport in the blood produces H^+ ions, making it sensitive to pH.

$$HHb^+(aq) + O_2(aq) \rightleftharpoons H^+(aq) + HbO_2(aq)$$

Hemeglobin acts as a buffer to help control the pH of the blood and allows carbon dioxide to return in the bloodstream to the lungs without upsetting the pH of the blood.

Hemeglobin is a protein with basic functional groups that enable it to accept H^+ ions after it has given up its oxygen in the cells, forming HHb^+. The pH of blood must be buffered to stay between 7.35 and 7.45 for the healthy function of cells.

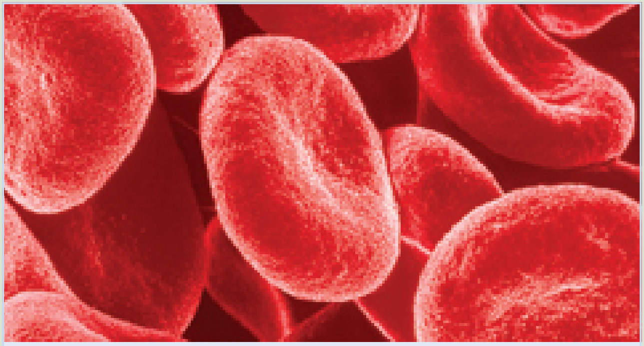

Figure 7.3.1 Red blood cells are packed with hemeglobin and have a large surface area for gas exchange.

The addition of the salt to the weak acid produces a mixture that has equally high proportions of HA(aq) and $A^-(aq)$.

When a small amount of an acid is added to the buffer solution, the pH initially *decreases*. The conjugate base ions, A^-, react with the added H^+ ions, causing the pH to increase again to the original value.

$$A^-(aq) + H^+(aq) \rightarrow HA(aq)$$

When a small amount of a base is added to the buffer solution, the pH initially increases, as $H^+(aq)$ is removed from the solution by reaction with $OH^-(aq)$.

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

The weak acid dissociates to increase $[H^+(aq)]$ and hence to decrease the pH to its original value.

$$HA(aq) \rightarrow H^+(aq) + A^-(aq)$$

If a large amount of acid or base is added to the buffer solution, there is not enough of the conjugate base ions or of the acid respectively to react and hence restore the pH to its original value, so the buffer is rendered ineffective.

A **basic buffer solution** is made up in the same way as the acidic buffer solution, but a weak base and the salt formed by the reaction between a strong acid and the weak base are the components of the solution (e.g. ammonia, NH_3, and ammonium chloride, NH_4Cl).

The equilibrium of the weak base is:

$$\underset{\substack{\text{weak}\\\text{base}}}{B(aq)} + H_2O(l) \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{BH^+(aq)} + OH^-(aq)$$

As in the case of the weak acid, this equilibrium lies significantly to the left-hand side, with a larger proportion of reactants (weak base) present than products.

The salt may be represented as BHX where X^- is a negative ion from a strong acid and BH^+ is the conjugate acid of the weak base, B. The salt could be formed by the reaction between a strong acid such as HCl and a weak base such as NH_3.

DEMO 7.1
Buffer solutions

$$\underset{\substack{\text{strong}\\\text{acid}}}{HX(aq)} + \underset{\substack{\text{weak}\\\text{base}}}{B(aq)} \rightarrow \underset{\text{salt}}{BHX(aq)}$$

The salt then dissociates completely:

$$BHX(aq) \rightarrow BH^+(aq) + X^-(aq)$$

The addition of the salt to the weak base produces a mixture that has equally high proportions of B(aq) and $BH^+(aq)$.

When a small amount of an acid is added to the buffer solution, the pH initially decreases. The weak base, B, reacts with the added H^+ ions, causing the pH to increase and to be restored to its original value.

$$B(aq) + H^+(aq) \rightarrow BH^+(aq)$$

When a small amount of a base is added to the buffer solution, the pH initially increases due to the reaction between $OH^-(aq)$ and $H^+(aq)$.

$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

The conjugate acid, BH^+, dissociates to supply $H^+(aq)$ ions and decrease the pH to its original value.

$$BH^+(aq) \rightarrow H^+(aq) + B(aq)$$

TABLE 7.3.1 SUMMARY OF COMPOSITION AND BEHAVIOUR OF BUFFER SOLUTIONS

Buffer solution	Made up of		When small amount of acid added	When small amount of base added
Acidic	Weak acid, e.g. ethanoic acid, CH_3COOH	Conjugate base of weak acid, e.g. sodium ethanoate, CH_3COONa	• pH initially decreases • Conjugate base reacts $A^-(aq) + H^+(aq) \rightleftharpoons HA(aq)$ • pH increases as H^+ reacts.	• pH initially increases $H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$ • Weak acid dissociates $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ • pH decreases as HA dissociates
Basic	Conjugate acid of weak base, e.g. ammonium chloride, NH_4Cl	Weak base,e.g. ammonia, NH_3	• Weak base reacts $B(aq) + H^+(aq) \rightleftharpoons BH^+(aq)$ • pH increases as H^+ reacts	• pH initially increases • Conjugate acid dissociates $BH^+(aq) \rightleftharpoons H^+(aq) + B(aq)$ • pH decreases as conjugate acid dissociates

Specific examples of buffer solutions

Figure 7.3.2 Buffer action can be illustrated by comparing the addition of acid to (a) a buffer solution and (b) a solution containing only ethanoic acid.

AS 18.2.2
Solve problems involving the composition and pH of a specified buffer system.
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An acidic buffer solution can be made up of a weak acid and its salt. One of the most common examples of this is ethanoic acid and sodium ethanoate. If 50 cm^3 of 0.1 mol dm^{-3} ethanoic acid is added to 50 cm^3 of 0.1 mol dm^{-3} sodium ethanoate solution a buffer solution will be created. The same buffer solution can also be prepared by adding 100 cm^3 of 0.1 mol dm^{-3} ethanoic acid to 50 cm^3 of 0.1 mol dm^{-3} sodium hydroxide. The sodium hydroxide and ethanoic acid will react to make the salt, sodium ethanoate, according to the equation:

$$NaOH(aq) + CH_3COOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

The excess of ethanoic acid provides the weak acid component of the buffer solution, so the final solution will have equal concentrations of ethanoic acid and sodium ethanoate.

Any combination of a weak acid and its salt can be used to make a buffer solution, the pH of which depends on the identity of the weak acid. This will be discussed in the next section.

A basic buffer solution is made up of a weak base and its salt, or, as described above for the acidic buffer solution, a 2 : 1 mixture of a weak base and a strong acid of equal concentrations can be used. Ammonia is a weak base that is commonly used for buffer solutions. The salt of its conjugate acid is usually ammonium chloride. This buffer solution could be made up by combining 50 cm^3 of 0.1 mol dm^{-3} ammonia solution with an equal volume of 0.1 mol dm^{-3} ammonium chloride solution, or 100 cm^3 of 0.1 mol dm^{-3} ammonia solution could be mixed with 50 cm^3 of 0.1 mol dm^{-3} hydrochloric acid. The excess ammonia would react with the hydrochloric acid to form ammonium chloride according to the equation:

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

The excess of ammonia provides the weak base component of the buffer solution, so the final solution will have equal concentrations of ammonia and ammonium chloride.

The pH of a buffer solution

Let us consider a buffer solution made up of a weak acid, HA, with the salt of its conjugate base, MA, dissolved in the solution. The acid dissociation constant, K_a for this weak acid will be

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

If we are to determine the pH of a solution, $[H_3O^+]$ will be most useful to us; so this relationship should be rearranged to give

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

As K_a is an equilibrium constant, these concentrations should be equilibrium concentrations; however, here an assumption is made on the basis of the composition of the buffer solution.

Due to the presence of the salt in the buffer solution, there is a large reservoir of $A^-(aq)$ present that pushes the acid dissociation equilibrium considerably to the left:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

This means that we can assume that the concentration of HA at equilibrium is essentially equal to the initial concentration of HA; that is, the concentration of the weak acid in the buffer solution.

$$[HA]_{eq} \cong [HA]_i = [acid]$$

Similarly, the concentration of the conjugate base ion, A^-, at equilibrium will be equal to the initial concentration of A^-,which is the anion of the salt in the buffer solution. In cases that you will encounter in this course, the concentration of the anion will be equal to the concentration of the salt.

$$[A^-]_{eq} \cong [A^-]_i = [salt]$$

Our expression for $[H_3O^+]$ is now simplified:

$$[H_3O^+] = K_a \times \frac{[acid]}{[salt]}$$

$$\mathbf{pH = p\mathit{K}_a + \log_{10} \frac{[salt]}{[acid]}}$$

Note that $[H_3O^+]$ depends on the ratio of [acid] to [salt] and on K_a, which is only temperature dependent. If the buffer solution is diluted at constant temperature, there is no effect on its pH.

If [acid] = [salt], there is a further simplification and we find that:

$$[H_3O^+] = K_a$$

and $pH = pK_a$

For a basic buffer solution a similar relationship exists.

For the equation

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

so $[OH^-] = K_b \times \frac{[B]}{[HB^+]}$

and

$$\mathbf{pOH = p}\boldsymbol{K_b} \mathbf{+ \log_{10} \frac{[salt]}{[base]}}$$

When [base] = [salt] this simplifies to $pOH = pK_b$.

To find pH use $pH = K_w - pOH$.

Worked example 1

Calculate the pH of a buffer solution containing 0.0500 mol dm^{-3} of ethanoic acid ($K_a = 1.74 \times 10^{-5}$ mol dm^{-3}) and 0.075 mol dm^{-3} sodium ethanoate.

Solution

$$\begin{aligned} pK_a(\text{ethanoic acid}) &= -\log_{10} 1.74 \times 10^{-5} \\ &= 4.76 \end{aligned}$$

[acid] = [ethanoic acid] = 0.0500 mol dm^{-3}

[salt] = [sodium ethanoate] = 0.075 mol dm^{-3}

$$\begin{aligned} pH(\text{buffer}) &= pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.76 + \log_{10}\left(\frac{0.0750}{0.0500}\right) \\ &= 4.76 + 0.176 \text{ (3 significant figures)} \\ &= 4.94 \end{aligned}$$

Worked example 2

Calculate the pH at 298 K of a mixture of 100 cm^3 of 0.10 mol dm^{-3} ammonia solution and 100 cm^3 of 0.050 mol dm^{-3} hydrochloric acid solution, pK_b(ammonia) = 4.75.

Solution

A reaction occurs between $NH_3(aq)$ and $HCl(aq)$ to make the salt, NH_4Cl, required for the buffer solution.

$$NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$$

$$n(NH_3) = cV = 0.10 \times 0.100 = 0.010 \text{ mol}$$

$$n(HCl) = cV = 0.050 \times 0.100 = 0.0050 \text{ mol}$$

HCl is the limiting reagent, so $n(NH_4Cl) = 0.0050$ mol

$n(NH_3)$ in excess = 0.010 – 0.0050 = 0.0050 mol

$$[NH_4] = \frac{n}{V} = \frac{0.0050}{0.200} = 0.025 \text{ mol dm}^{-3}$$

$$[NH_4Cl] = \frac{n}{V} = \frac{0.0050}{0.200} = 0.025 \text{ mol dm}^{-3} = [NH_3]$$

Since $[NH_4Cl] = [NH_3]$

$$\begin{aligned}[OH^-] &= K_b \times 1 \\ pOH &= pK_b \\ &= 4.75 \\ pH &= K_w - pOH \\ &= 14 - 4.75 \\ &= 9.25\end{aligned}$$

Worked example 3

Deduce the concentrations of solutions required to make a buffer solution of pH = 4.5 using benzoic acid and sodium benzoate, pK_a(benzoic acid) = 4.20.

Solution

$$pH = pK_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$4.5 = 4.20 + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

$$\log_{10}\frac{[\text{salt}]}{[\text{acid}]} = 0.30$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 10^{0.30}$$

$$\frac{[\text{salt}]}{[\text{acid}]} = 2.0$$

To make a buffer solution of pH = 4.5 using benzoic acid and sodium benzoate, the concentration of the salt, sodium benzoate, will need to be double that of the benzoic acid. For example the buffer could be made up of a 0.050 mol dm^{-3} solution of benzoic acid and a 0.10 mol dm^{-3} solution of sodium benzoate.

How effective is a buffer solution?

While the ability of a buffer solution to resist changes in pH upon the addition of an amount of an acid or alkali can be shown experimentally, it can also be shown by a series of calculations. Such calculations provide quite an elegant proof of experimental observation.

Consider the following experiment.

A buffer solution has a pH of 4.5 and has been prepared, as in the example above, using 0.050 mol dm^{-3} benzoic acid and 0.10 mol dm^{-3} sodium benzoate solutions. What happens if 1.0 cm^3 of 1.0 mol dm^{-3} sodium hydroxide solution is added to 500 cm^3 of the buffer solution?

The initial pH of the buffer solution is 4.5. The addition of the sodium hydroxide solution causes the acid concentration to fall and the concentration of the salt (represented by the anion $C_6H_5COO^-$) to increase due to the reaction:

$$OH^-(aq) + C_6H_5COOH(aq) \rightarrow C_6H_5COO^-(aq) + H_2O(l)$$

The amount of OH^- in 1.0 cm^3 of 1.0 mol dm^{-3} NaOH can be calculated:

$$n(OH^-) = cV = 1.0 \times 0.0010 = 0.0010 \text{ mol}$$

$n(C_6H_5COOH)$ that reacts with this amount of OH^- = 0.0010 mol

The solution originally contained 0.050 × 0.500 = 0.025 mol of benzoic acid.

The new concentration of the acid is given by:

$$\begin{aligned}[C_6H_5COOH] &= \frac{(0.025 - 0.0010)}{0.50} \\ &= 0.048 \text{ mol dm}^{-3}\end{aligned}$$

As the reaction of C_6H_5COOH with OH^- produces $C_6H_5COO^-$, the amount of benzoate ions increases by 0.0010 mol.

$$n(C_6H_5COO^-)\text{initially} = 0.10 \times 0.500 = 0.050 \text{ mol}$$

The new concentration of benzoate ions in the buffer solution is given by

$$[C_6H_5COO^-] = \frac{(0.050 + 0.0010)}{0.50} = 0.102 \text{ mol dm}^{-3}$$

(Note that the slight increase in volume of the solution due to the addition of 1 cm^3 NaOH solution has been ignored since its impact on the final answers is negligible.)

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.2 + \log_{10}\left(\frac{0.102}{0.048}\right) \\ &= 4.53\end{aligned}$$

While a slight increase (+0.03 units) in pH has occurred, this is not likely to make a great difference to the system.

If we compare the change in pH if the same amount of sodium hydroxide had been added to a solution of hydrochloric acid with pH = 4.5 we will see a very different situation:

$$\begin{aligned}[H_3O^+] &= 10^{-4.5} \\ &= 3.16 \times 10^{-5} \text{ mol dm}^{-3}\end{aligned}$$

In 500 cm^3 of this solution there are $3.16 \times 10^{-5} \times 0.500 = 1.58 \times 10^{-5}$ mol of H_3O^+ ions that will react with the 0.0010 mol of NaOH added to it.

$$\begin{aligned}n(OH^-) &= 0.0010 - 1.58 \times 10^{-5} \\ &= 9.84 \times 10^{-4} \text{ mol}\end{aligned}$$

$$\begin{aligned}[OH^-] &= \frac{9.84 \times 10^{-4}}{0.500} \\ &= 1.97 \times 10^{-3} \text{ mol dm}^{-3} \\ \text{pOH} &= -\log_{10} 1.97 \times 10^{-3} \\ &= 2.71 \\ \text{pH} &= 14 - 2.71 \\ &= 11.29\end{aligned}$$

This is a change of nearly 7 pH units—a huge difference when compared with the change of 0.3 units (4.50 to 4.53) to the buffer solution!

THEORY OF KNOWLEDGE

A probe determines the pH of an acidic buffer made from 0.0500 mol dm^{-3} ethanoic acid and 0.0750 mol dm^{-3} sodium ethanoate to be 4.94. But, will a benzoic acid–sodium benzoate buffer of the same concentrations have exactly the same pH? To answer this question the buffer could be made in the lab and its pH tested. Alternatively, deductive reasoning using mathematics could be used. The first step involves making a series of premises—statements or givens that are assumed to be true. The premises are the starting point for the proof, the step-by-step logical method of justification that leads to a specific conclusion.

Premises

1 $K_a = \frac{[A^-][H_3O^+]}{[HA]}$

$[HA]_{eq} = [HA]_i = [acid]$

2 $[A^-]_{eq} = [A^-]_i = [salt]$

Proof

pK_a(benzoic acid) = 4.20

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

$$\begin{aligned} pH &= pK_a + \log_{10}\frac{[A^-]}{[HA]} \\ &= 4.20 + \log_{10}\left[\frac{0.0750}{0.0500}\right] \\ &= 4.20 + 0.176 \\ &= 4.38 \end{aligned}$$

Conclusion

The two buffers do not have exactly the same pH.

- Can a mathematical proof using deductive reasoning give greater certainty to experimental observations? Explain.
- What is the role of inductive reasoning in establishing a mathematical claim in science?
- A mathematical proof is called ‘elegant’ or ‘beautiful’ if, in addition to being a sound argument it is a pleasure to solve, incisive, ingenious, uses as few steps as possible and has an unexpected element of surprise. Can you name any elegant proofs in chemistry or mathematics?

Section 7.3 Exercises

1 An aqueous solution containing 0.1 mol dm^{-3} ammonia and 0.1 mol dm^{-3} ammonium chloride acts as a buffer with a pH of 9.3.

a Define a buffer solution.

b Using equations, explain what happens in this buffer solution when a small amount of:

i HCl is added

ii NaOH is added.

2 **a** Describe the composition of an acid buffer solution in general terms.

b State the names of two compounds, one of which is a base, which could be used to prepare an acid buffer solution.

3 Suggest the identity of an acid and the amount of it that could be added to 50 cm^3 of a solution containing 0.20 mol ammonia in order to prepare a buffer solution.

4 Compare an acidic buffer solution and a basic buffer solution.

5 Describe one use of buffer solutions in the human body.

6 Calculate the pH at 25°C of a buffer solution composed of 0.045 mol dm^{-3} propanoic acid ($K_a = 1.35 \times 10^{-5}$) and 0.12 mol dm^{-3} sodium propanoate.

7 Calculate the pH of a buffer solution composed of 0.10 mol dm^{-3} ammonia ($pK_b = 4.75$) and 0.20 mol dm^{-3} ammonium chloride.

8 Explain, using a chemical equation to aid your answer, why a mixture of 50 cm^3 of 0.10 mol dm^{-3} ammonia solution and 50 cm^3 of 0.10 mol dm^{-3} hydrochloric acid cannot be used as a buffer solution.

9 Calculate the pH of a mixture of 75 cm^3 of methanoic acid solution of concentration 0.10 mol dm^{-3} and 75 cm^3 of sodium hydroxide solution of concentration 0.050 mol dm^{-3} (pK_a (methanoic acid) = 3.75).

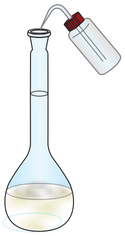
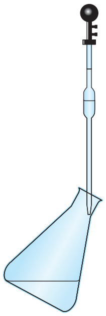
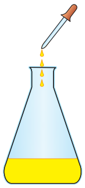
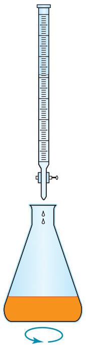
10 Deduce the concentrations of solutions required to make a buffer solution of pH = 5.0 using ethanoic acid and sodium ethanoate. pK_a(ethanoic acid) = 4.76.

7.4 ACID–BASE TITRATIONS

Interactive Animation
Acid–base titration

The type of experiment in which the concentration of an acid or a base can be found is known as a volumetric analysis. Let us consider the procedure used in a typical volumetric analysis (see table 7.4.1). In the following example, we determine the ammonia content of a window cleaner solution by titrating with a standardized hydrochloric acid solution.

TABLE 7.4.1 VOLUMETRIC ANALYSIS OF THE AMMONIA CONTENT OF A WINDOW CLEANER

Procedure	Explanation
Rinse and fill a 10 cm^3 pipette with window cleaner solution.	The volume of the sample must be determined accurately.
Transfer the sample to a 250.0 cm^3 volumetric flask. Make the volume up to the calibration mark with distilled water. 	Direct titration of the window cleaner would require a large volume of acid to be used. The cleaner is therefore diluted to form a stock solution.
Rinse and fill a 20.00 cm^3 pipette with the diluted cleaner. Transfer the 20.00 cm^3 aliquot to a conical flask. 	An accurately measured, known volume of cleaner solution is obtained. Rinsing the pipette with cleaner solution ensures that the solution is not diluted by water droplets.
Add several drops of methyl orange indicator. 	The indicator will change colour when the reaction is complete.
Rinse and fill a burette with a standardized 0.108 mol dm^{-3} HCl solution.	Rinsing ensures that the HCl solution is not diluted by water droplets in the burette.
Record the initial burette reading. Titrate the cleaner solution with HCl solution until the **endpoint** (colour change to orange) is reached. Record the final burette reading. 	The colour change (endpoint) occurs very close to the point at which the reaction is complete (equivalence point). Subtraction of the initial reading from the final reading gives the volume of HCl added (the titre).
The titration process is repeated until **concordant** titres are obtained.	Repeating the process until reasonably consistent titres are obtained allows an averaging of results. Concordant titres are those within a specified range, e.g. within the random error of the glassware, of each other.

PRAC 7.2
Determining the ammonia content of a window cleaner using a standardized HCl solution

Worked example 1

The following results were obtained during a titration experiment to determine the ammonia content of a window cleaner, as described in table 7.4.1. Calculate the concentration of ammonia in the window cleaner in mol dm^{-3}.

Volume of cleaner used:	10.0 cm^3
Volume of diluted solution:	250.0 cm^3
Aliquot of diluted solution used:	20.00 cm^3
Concentration of HCl solution:	0.108 mol dm^{-3}
Indicator:	Methyl orange
Average volume of HCl solution used:	24.93 cm^3

Solution

Step 1: Write a balanced equation.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

Step 2: Calculate the amount (in mol) of the known substance.

$$n(HCl) = cV = 0.108 \times 24.93 \times 10^{-3} = 2.692 \times 10^{-3} \text{ mol}$$

Step 3: Determine the mole ratio of the unknown substance to the known substance.

$$n(NH_3) = n(HCl) = 2.692 \times 10^{-3} \text{ mol}$$

Step 4: Allow for dilution.

$$n(NH_3)_{\text{original}} = 2.692 \times 10^{-3} \times \frac{250.0}{20.0} = 0.0337 \text{ mol}$$

Step 5: Solve for the required quantity (in the required units).

$$\text{Concentration of } NH_3 \text{ in window cleaner} = \frac{n}{V} = \frac{0.0337}{0.0100} = 3.37 \text{ mol dm}^{-3}$$

CHEM COMPLEMENT

Hazardous cleaners

Mixing household cleaners can be quite hazardous. Mixing hypochlorite bleach (ClO^-) with ammonia cleaners is extremely hazardous. The products of this reaction include gaseous chloramine (NH_2Cl) and hydrazine (NH_2NH_2), both of which are highly toxic. Similarly, mixing bleach with toilet bowl cleaners containing hydrochloric acid results in the formation of poisonous chlorine gas (Cl_2). Generating these toxic gases in limited, often poorly ventilated bathroom spaces can be extremely hazardous. Never mix chemicals (even household cleaners) without specific directions to do so.

AS 18.4.1
Sketch the general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases, and explain their important features. © IBO 2007

Titration curves

A titration curve is a graph of pH against volume of solution added for a titration involving strong and weak acids and bases. In any titration the initial solution is either the acid or the base that is being analysed, so the pH at the beginning of the pH curve (at volume = 0 cm^3) is equal to that of the solution in the flask. This information is a good starting point for determining the nature of the solutions that are reacting. If the initial pH is very low, say pH = 1, then the solution being titrated is a strong acid. If the initial pH is somewhat higher than this, but still below pH = 7, then the solution being titrated is a weak acid. In the event that an alkali is being analysed, the initial pH may be about 10 or 11 (weak base) or much higher, say pH = 13 for a strong base.

QuickTime Video
Acid–base titration

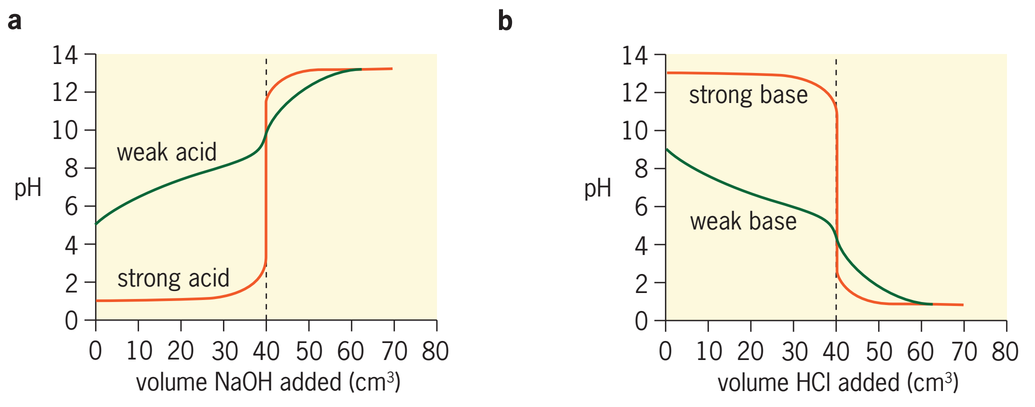


Figure 7.4.1 The initial pH identifies the solution being analysed as (a) a strong or weak acid or (b) a strong or weak base.

During a titration, the pH of the solution in the reaction flask does not change in a regular manner as more solution is added from the burette. To investigate the shape of this type of graph more closely, we will use the graph of pH for the titration of 20.00 cm^3 of 0.10 mol dm^{-3} HCl with 0.10 mol dm^{-3} NaOH in figure 7.4.2.

PRAC 7.3
Using data-logging equipment to graph an acid–base titration

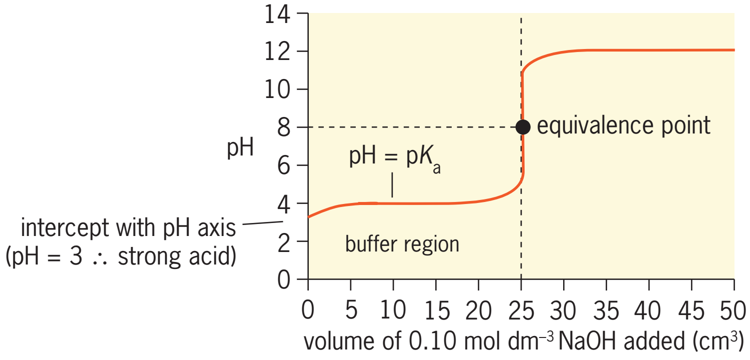


Figure 7.4.2 The important parts of a graph of pH against volume for the titration of CH_3COOH with NaOH.

Initially, the pH of the flask contents will be 3.0 because CH_3COOH is a weak acid and the pH of a 0.10 mol dm^{-3} CH_3COOH solution equals 3. As NaOH is added, the pH rises slowly at first. This almost horizontal part of the curve is known as the **buffer region**. It represents a solution that has acid and a solution of the salt present. At the point in this region where the amount of base that has been added is equal to half the amount that is required to neutralize the acid we would say that the acid has been **half neutralized**. The solution is a buffer solution with [acid] = [salt] and pH = pK_a(acid). If an acid is being added to a base, at this point when [base] = [salt] the pOH will equal pK_b (see section 7.3, p. 212).

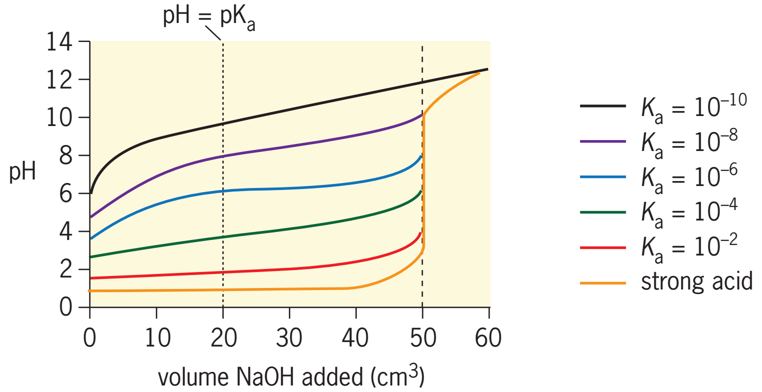


Figure 7.4.3 When the acid is half neutralized, pH = pK_a. This can be seen in the titration curves for six acids with differing K_a values. Note the difference in the shape of the curve as K_a changes.

After the buffer region, the pH rises very sharply and passes through the **equivalence point** (the point at which the acid and base have reacted in exact stoichiometric amounts). The equivalence point is found halfway along the vertical section of the graph. At the equivalence point of this graph, the pH is 7, because the solution contains water, sodium ions and chloride ions only—all neutral species. The pH at the equivalence point varies, depending on the titration being performed, as we will see later. Beyond the equivalence point, as more NaOH is added, the pH rises slowly again.

The combination of strong and weak acid and base involved in a titration governs the shape of the graph of pH against volume, a **titration curve**. Figure 7.4.4 shows a typical titration curve for the addition of a strong base to a strong acid. Notice that at near the equivalence point the pH rises sharply from pH = 3 to pH = 11. The sudden change in pH at that point could occur with the addition of as little as one drop of NaOH solution. If the strong acid was being added to a strong base, this graph would have the same shape, but would start at a high pH, drop sharply between pH = 11 and pH = 3 and level out in the last part of the graph. Note that this later part of the pH curve is of little use in analysing an acid or a base, except perhaps to identify the solution being added, if it is unknown.

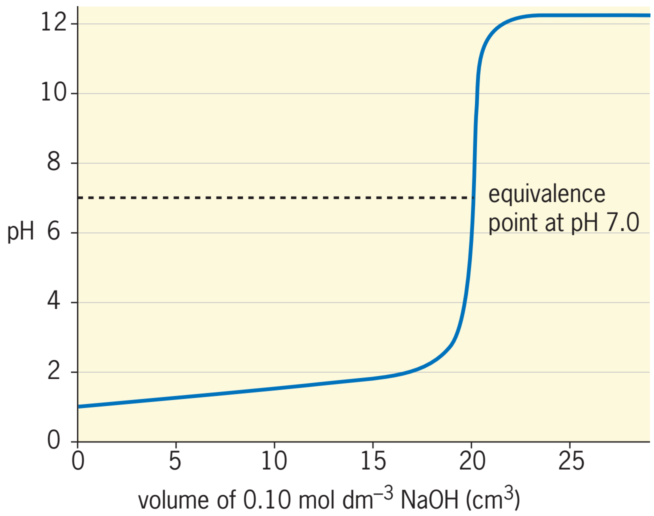


Figure 7.4.4 Titration curve for a strong acid with a strong base.

If the acid being used for the titration is a weak acid, the shape of the titration curve differs significantly. Consider the graph shown in figure 7.4.5 for the titration of 20.00 cm^3 of 0.10 mol dm^{-3} ethanoic acid (CH_3COOH) with 0.10 mol dm^{-3} NaOH. Ethanoic acid is a weak acid. The product of its reaction with NaOH is a weak base, the ethanoate ion (CH_3COO^-). At the equivalence point of this titration, the products in the reaction flask will include this weak base; hence, the pH will be greater than 7, due to the reaction of the ethanoate ion with water:

$$CH_3COO^-(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + OH^-(aq)$$

Note that in figure 7.4.5 the pH change near the equivalence point is sharp, but the pH at the equivalence point is greater than 7.

Prac 7.4
Determining the ethanoic acid content of vinegar

Interactive Animation
Titration curve for a weak acid with a strong base

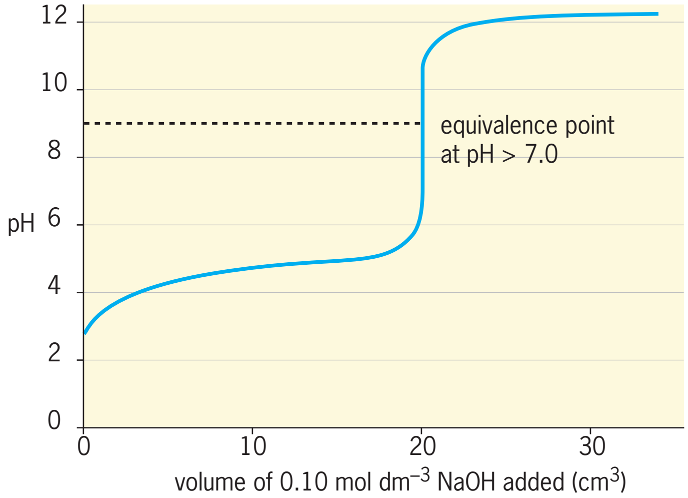


Figure 7.4.5 Titration curve for a weak acid with a strong base.

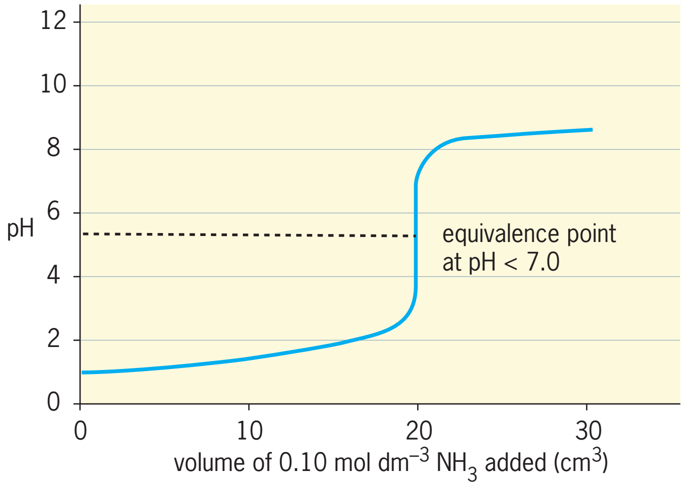


Figure 7.4.6 Titration curve for a strong acid with a weak base.

How does the shape of the titration curve change if a strong acid and a weak base are used? Figure 7.4.6 shows the graph for the titration of 20.00 cm^3 of 0.10 mol dm^{-3} HCl with 0.10 mol dm^{-3} ammonia (NH_3). Ammonia is a weak base. The product of its reaction with HCl is a weak acid, the ammonium ion (NH_4^+). At the equivalence point of this titration, the products will include this weak acid, hence the pH will be less than 7, due to the reaction of the ammonium ion with water:

$$NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$$

In the final case of a weak acid–weak base titration with the graph shown in figure 7.4.7, the pH increases steadily and does not change rapidly at the equivalence point. Determining the equivalence point using an indicator is therefore difficult. In this case, the titration must be followed using a pH meter, and the titration curve used to determine the equivalence point.

Worksheet 7.3
Acid–base titrations

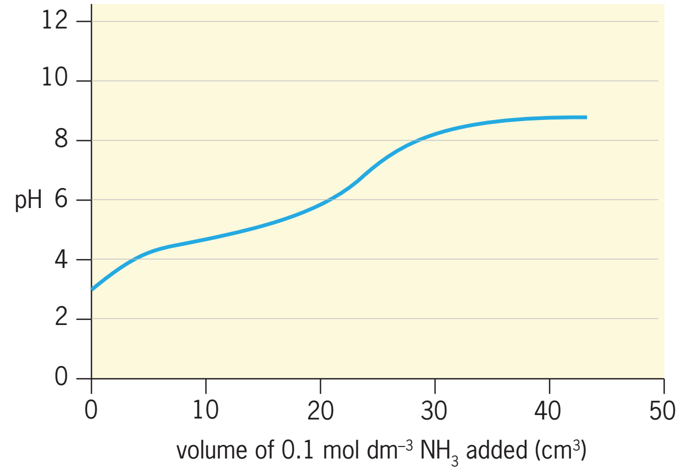


Figure 7.4.7 Titration curve for a weak acid with a weak base.

Back titrations

In some situations, it is not possible to conduct a volumetric analysis as described above. Where the substance to be analysed is insoluble, such as limestone ($CaCO_3$), direct titration is not possible.

Titration is also not possible if the solution being analysed is volatile. In that case, with evaporation occurring, the titration method is not fast enough to carry out the analysis before the concentration of the solution changes. Weak acids and weak bases also present problems, as the pH does not change rapidly at the equivalence point.

Determining the equivalence point using an indicator is therefore difficult. In each of these situations, the technique known as a **back titration** (or indirect titration) can be used. A back titration involves adding a measured excess of reagent to the sample being analysed.

A reaction occurs completely and usually quickly, and an amount of unreacted reagent remains in the solution. This unreacted amount is then determined by direct titration. The determination of the $CaCO_3$ content of eggshells illustrates the procedures used in a back titration (see table 7.4.2).

Worksheet 7.4
A back titration

TABLE 7.4.2 DETERMINING $CaCO_3$ CONTENT OF EGGSHELLS BY BACK TITRATION

Procedure	Explanation
Accurately weigh approximately 1 g of clean dry eggshells. Crush the shells and transfer them to a conical flask.	Mass of the sample must be determined. The sample is crushed to allow faster, more complete reaction of the $CaCO_3$ in the shells with the hydrochloric acid.
Add an aliquot of standardized hydrochloric acid solution.	This is a measured excess of reactant. Reaction occurs according to: $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$
Allow the mixture to stand until no more bubbles of CO_2 evolve.	This ensures the reaction is complete; that is, all the $CaCO_3$ has reacted. Unreacted HCl remains in the flask.
Rinse and fill a burette with standardized NaOH solution. Add several drops of methyl red indicator to the flask.	The unreacted acid is to be titrated with NaOH. The indicator changes colour when the reaction is complete. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$
Titrate the solution until the endpoint (colour change) is reached. Record the titre of NaOH used.	The amount of NaOH reacting is determined. This allows the amount of unreacted HCl to be determined, which in turn allows the amount of reacted HCl to be determined.

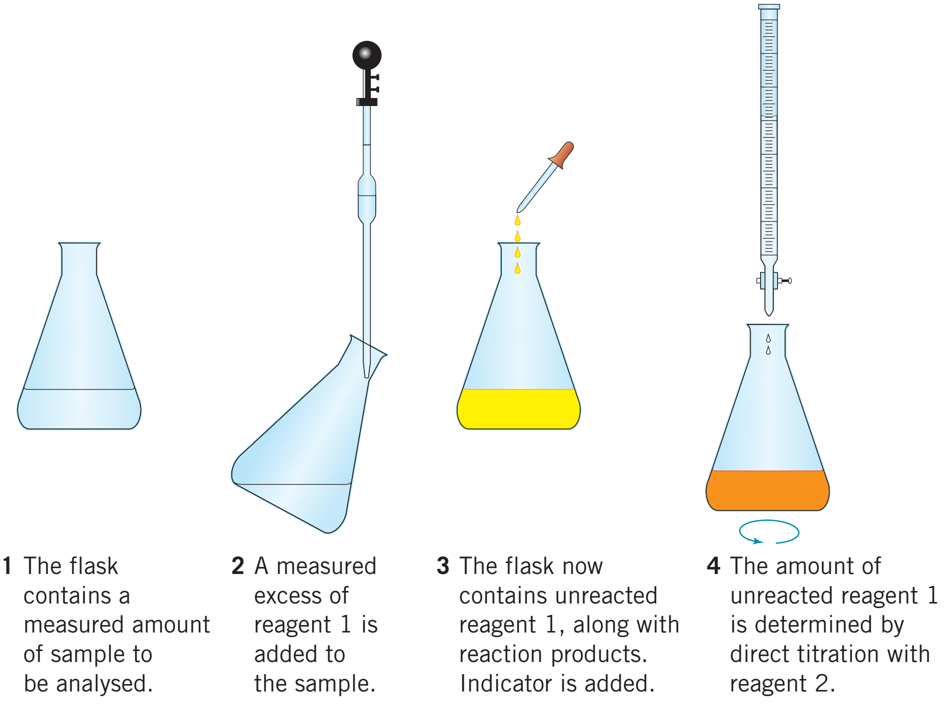


Figure 7.4.8 The key steps in a back titration.

THEORY OF KNOWLEDGE

Many people commonly believe that the pain caused by a wasp or bee sting can be reduced by neutralizing it. Wasp sting venom is alkaline and so its effects can be neutralized with an acid such as vinegar; bee sting venom is acidic and so its effects can be neutralized with an alkali such as baking soda. Consider the following claim made in an IB Chemistry exam.

Carbonic acid can be used to treat wasp stings.

IB Chemistry SL Exam, Paper 2, Nov 2002

- Usually we believe some knowledge claims over others because we have a good reason for doing so; we have a justification for that belief. Identify some of the different ways of justifying the truth of this claim. Consider direct experience, reasoning, expert opinion, general consensus, primary sources and memory.
- Which of these methods of justification give the strongest and weakest reasons for believing?

Prac 7.5 Determining the nitrogen content of a fertilizer

Worked example 2

The $CaCO_3$ content of an eggshell sample was determined by a back titration method as described in table 7.4.2. The results of the back titration were:

Mass of eggshell sample:	0.692 g
Concentration of HCl solution:	0.400 mol dm^{-3}
Volume of HCl solution added to sample:	20.00 cm^3
Concentration of NaOH solution:	0.152 mol dm^{-3}
Titre of NaOH solution:	22.21 cm^3

Solution

Calculate the amount of HCl added initially:

$$n(\mathrm{HCl})_{\mathrm{initially}} = cV = 0.400 \times 20.00 \times 10^{-3} = 8.00 \times 10^{-3} \text{ mol}$$

This is an excess of HCl. Some of it reacted with $CaCO_3$ in the eggshell and the remaining HCl (now called 'unreacted') was then titrated with NaOH.

Calculate the amount of 'unreacted' HCl:

$$\mathrm{HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)}$$

$$n(\mathrm{NaOH}) = cV = 0.152 \times 22.21 \times 10^{-3} = 3.38 \times 10^{-3} \text{ mol}$$

$$n(\mathrm{HCl})_{\mathrm{unreacted}} = n(\mathrm{NaOH}) = 3.38 \times 10^{-3} \text{ mol}$$

Calculate the amount of HCl that reacted with the eggshells:

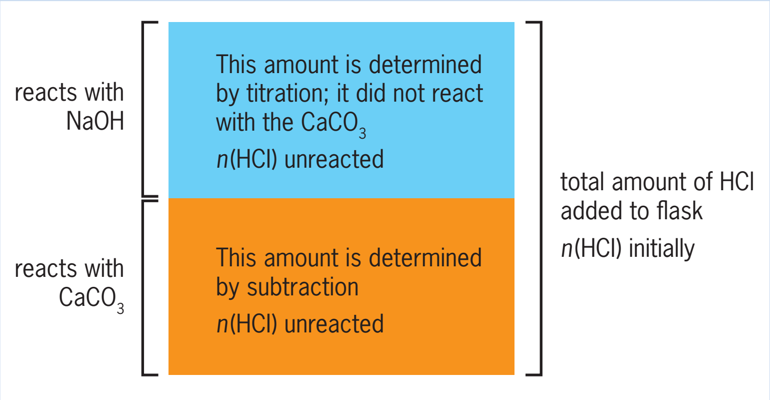


Figure 7.4.9 The above diagram may help you visualize the total amount of HCl used and how it relates to the amount of HCl that reacted with the $CaCO_3$.

$$\begin{aligned} n(\mathrm{HCl})_{\mathrm{reacted}} &= n(\mathrm{HCl})_{\mathrm{initially}} - n(\mathrm{HCl})_{\mathrm{unreacted}} \\ &= 8.00 \times 10^{-3} - 3.38 \times 10^{-3} = 4.62 \times 10^{-3} \text{ mol} \end{aligned}$$

Calculate the amount of $CaCO_3$ that reacted with HCl:

$$\mathrm{CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)}$$

$$n(\mathrm{CaCO_3}) = \tfrac{1}{2} \times n(\mathrm{HCl})_{\mathrm{reacting}} = \tfrac{1}{2} \times 4.62 \times 10^{-3} = 2.31 \times 10^{-3} \text{ mol}$$

Calculate the mass of $CaCO_3$ in the eggshells:

$$m(\mathrm{CaCO_3}) = n \times M = 2.31 \times 10^{-3} \times 100.09 = 0.231 \text{ g}$$

$$\% \text{ CaCO}_3 \text{ in eggshells} = \frac{m(\mathrm{CaCO_3})}{m(\text{eggshells})} \times \frac{100}{1} = \frac{0.213}{0.692} \times \frac{100}{1} = 33.4\%$$

Section 7.4 Exercises

1 20.00 cm^3 of vinegar was diluted to a volume of 100.0 cm^3 with distilled water. A 20.00 cm^3 sample of diluted vinegar was completely neutralized by 24.60 cm^3 of 0.200 mol dm^{-3} standardized NaOH solution. Calculate the ethanoic acid concentration of the vinegar.

2 Sodium phosphate (Na_3PO_4) is used commercially to clean greasy surfaces. The Na_3PO_4 content of a cleaner was analysed by titration with standardized 0.112 mol dm^{-3} hydrochloric acid. A 5.00 cm^3 sample of Na_3PO_4 cleaner required 21.03 cm^3 of acid for reaction according to the equation:

$$2HCl(aq) + Na_3PO_4(aq) \rightarrow 2NaCl(aq) + NaH_2PO_4$$

Determine the concentration of Na_3PO_4 in the cleaner.

3 Vitamin C ($C_6H_8O_6$) is a monoprotic acid. The vitamin C content of a tablet was determined by titration with NaOH solution. 0.300 g of a tablet required 19.62 cm^3 of 0.0832 mol dm^{-3} NaOH for complete reaction. Calculate the percentage by mass of vitamin C in the tablet.

4 A solution containing ammonia requires 18.0 cm^3 of 0.100 mol dm^{-3} hydrochloric acid to reach the equivalence point of a titration.

a Calculate the amount (in mol) of ammonia that reacts with the hydrochloric acid.

b Sketch a graph to show how the pH changes as hydrochloric acid is added to the ammonia solution. Use a pH scale of 0–14 and an acid volume scale of 0–25 cm^3.

c On the graph that you sketched in part **b**, label:

i the equivalence point

ii the point at which the ammonia is half neutralized.

d From your graph determine the pH of the solution at the equivalence point, and explain why the titration has an equivalence point with that value.

5 A 20.00 cm^3 solution containing hydrochloric acid, HCl, is titrated with 0.12 mol dm^3 sodium hydroxide, NaOH, solution.

a State the pH that you would expect at the equivalence point.

b If the equivalence point is reached after the addition of 15 cm^3 of the NaOH solution, determine the concentration of the HCl solution.

c State the pH of the HCl solution at the beginning of the titration (before any NaOH solution had been added).

d Sketch a graph to show how the pH changes as NaOH solution is added to the HCl solution.

e What volume of NaOH would have been added when the HCl had been half neutralized?

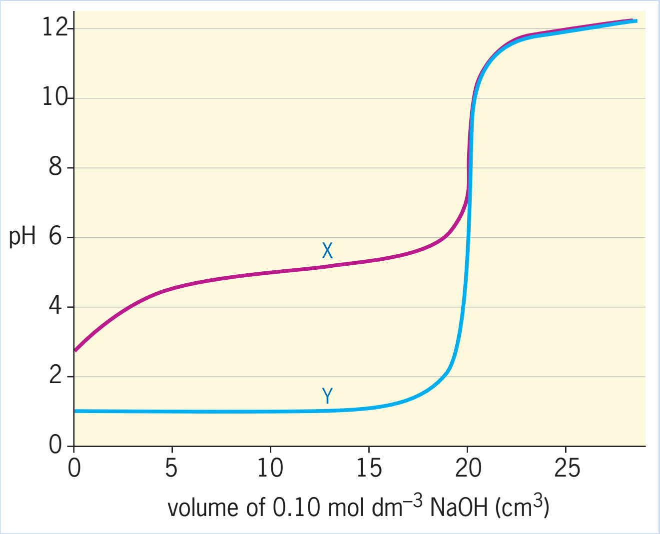
6 A 0.0100 mol dm^{-3} solution of sodium hydroxide is added to 20.0 cm^3 of a 0.00850 mol dm^{-3} solution of ethanoic acid.

a Determine the volume of sodium hydroxide solution required to completely neutralize the ethanoic acid solution.

b Estimate the pH of the solution at the equivalence point.

c Sketch a graph to show how the pH changes as sodium hydroxide solution is added to the ethanoic acid solution.

7 The following graph shows titration curves for two experiments. A 25.0 cm^3 aliquot of hydrochloric acid was titrated with a 0.100 mol dm^{-3} NaOH solution in one experiment. In the other, a 25.0 cm^3 aliquot of ethanoic acid of the same concentration as the hydrochloric acid, was titrated with a 0.100 mol dm^{-3} NaOH solution.



- **a** Determine which curve, X or Y, represents the experiment using the HCl solution.
- **b** Explain why the pH at the start of each curve is different.
- **c** Explain why the pH values at the equivalence points are different.
- **d** Use the titration curve to determine the pK_a of ethanoic acid.
- **e** Calculate the concentration of the acid solutions.

8 Distinguish between the terms *direct titration* and *back titration*.

9 A sample of lawn fertilizer was analysed by back titration to determine its ammonium ion (NH_4^+) content. The sample was boiled in NaOH solution. The reaction occurred according to the equation:

$$NH_4^+(aq) + NaOH(aq) \rightarrow NH_3(g) + H_2O(l) + Na^+(aq)$$

When evolution of the ammonia ceased, the solution was cooled and then titrated with HCl solution. The reaction occurred according to the equation:

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

The results of the analysis are given:

Mass of fertilizer sample:	0.104 g
Volume of NaOH solution:	25.00 cm^3
Concentration of NaOH solution:	0.120 mol dm^{-3}
Titre of HCl solution:	16.13 cm^3
Concentration of HCl solution:	0.100 mol dm^{-3}

Calculate the NH_4^+ content of the fertilizer (as % by mass).

7.5 SALT HYDROLYSIS

When an acid and a base react together a salt is formed. You will recall that the equivalence point in an acid–base titration, is the point at which the acid and base have reacted together in their correct stoichiometric ratio. The acid has been neutralized by the base, forming a salt that in solution has a pH equal to the pH at the equivalence point of the titration. This can be seen in figure 7.5.1. The reaction of a salt with water is known as **salt hydrolysis**.

AS 18.3.1
Deduce whether salts form acidic, alkaline or neutral aqueous solutions. © IBO 2007

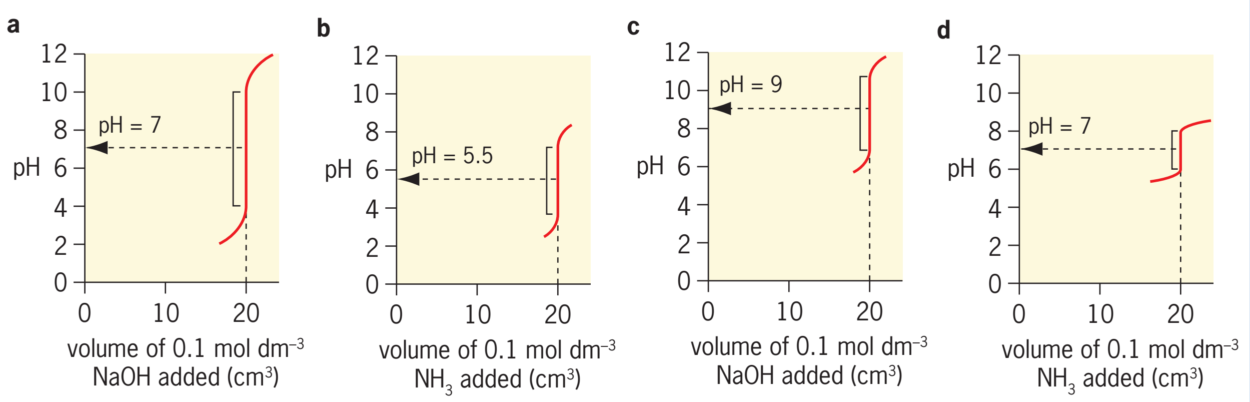


Figure 7.5.1 The pH of the salt formed during a titration is equal to the pH at the equivalence point. (a) Strong acid–strong base, (b) strong acid–weak base, (c) weak acid–strong base, and (d) weak acid–weak base.

To understand the acidic or basic nature of these salts we should look at their acid–base behaviour in aqueous solution.

DEMO 7.2
pH of salt solutions

1 Salt formed by reaction of a strong acid with a strong base, e.g. NaCl

In aqueous solution neither Na^+ nor Cl^- have the ability to behave as a Brønsted–Lowry acid or base. They have no affinity for H^+ ions, nor can they produce H^+ ions. As a result they have no effect on the $[H_3O^+]$ when dissolved in water, so they do not change the pH. It remains at 7.

2 Salt formed by reaction of a strong acid with a weak base, e.g. NH_4Cl

In aqueous solution, the NH_4^+ ion is the conjugate acid of the weak base NH_3, and Cl^- ion has no acid–base properties. The NH_4^+ ion can react with water (undergo hydrolysis):

$$NH_4^+(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NH_3(aq)$$

The production of $H_3O^+(aq)$ in this hydrolysis reaction makes the solution slightly acidic.

3 Salt formed by reaction of a weak acid with a strong base, e.g. CH_3COONa

In aqueous solution the Na^+ ion has no acid–base properties; however, the anion CH_3COO^- is the conjugate base of a weak acid. This makes it able to react with water:

$$CH_3COO^-(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + OH^-(aq)$$

The production of $OH^-(aq)$ in this hydrolysis reaction makes the solution of CH_3COONa slightly basic.

4 Salt formed by the reaction of a weak acid with a weak base, e.g. CH_3COONH_4

Both the cation and the anion have acid–base properties. The cation NH_4^+ is the conjugate acid of the weak base NH_3, and the anion CH_3COO^- is the conjugate base of the weak acid CH_3COOH. The pH of the salt solution will be determined by the relative strengths of the two ions. To do this, the K_a value for the acidic ion NH_4^+ can be compared with the K_b value for the basic ion CH_3COO^-. If the K_a value for the acidic ion is greater than the K_b value for the basic ions, the solution will be acidic. If the K_a value for the acidic ion is less than the K_b value for the basic ions, the solution will be basic. Equal K_a and K_b values mean a pH of 7.

Worked example 1

Determine whether a solution of the salt NH_4CN will be acidic, neutral or basic.

Solution

The K_a of NH_4^+ and the K_b of CN^- must be determined and then compared.

The K_a of the conjugate acid NH_4^+ can be found using $K_a \times K_b = K_w$ where K_b is the base dissociation constant of ammonia, and assuming that the temperature is 25°C.

$$K_a(NH_4^+) = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}\ \text{mol dm}^{-3}$$

CN^- is the conjugate base of HCN, so the K_b of CN^- is found using $K_a \times K_b = K_w$, where K_a is the acid dissociation constant of hydrogen cyanide, and assuming that the temperature is 25°C.

$$K_b(CN^-) = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.03 \times 10^{-10}} = 1.66 \times 10^{-5}\ \text{mol dm}^{-3}$$

The K_a value for NH_4^+ is less than the K_b value for CN^- so the solution will be basic.

Another type of salt hydrolysis

When a salt containing a small, highly charged metal ion such as aluminium nitrate, $Al(NO_3)_3$, is dissolved in water, the solution is significantly acidic. The aluminium ion has a sufficiently high charge that it attracts water molecules to itself as ligands, forming a hydrated complex ion, $[Al(H_2O)_6]^{3+}$, that is a weak acid (see chapter 3). Because the high charge on the metal ion polarizes the water ligands, they are able to donate hydrogen ions to free water molecules in the aqueous solution.

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq),\ K_a = 1 \times 10^{-5}\ \text{mol dm}^{-3}$$

The higher the charge on the metal ion, the stronger is the acidity of the hydrated ion. For example, the iron(III) ion, Fe^{3+}, also attracts and polarizes water molecules:

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightarrow [Fe(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq),\ K_a = 6 \times 10^{-3}\ \text{mol dm}^{-3}$$

Cations of group 1 and the heavier members of group 2 do not have a charge density large enough to attract water molecules in this way, so they do not affect the pH of an aqueous solution. Other metal ions, for example, the lighter members of group 2 such as Mg^{2+}, group 3 metal ions and the transition metal ions will lower the pH of an aqueous solution, although with less effect than the small, highly charged Al^{3+} and Fe^{3+} ions.

TABLE 7.5.1 SUMMARY OF SALT HYDROLYSIS

pH of solution	Neutral	Acidic	Basic	Depends on K_a and K_b
Combination of acid and base to make salt	Strong acid + strong base	Strong acid + weak base Or Strong acid anion + highly charged metal cation	Weak acid + strong base	Weak acid + weak base
Examples	NaCl KNO_3	NH_4NO_3 CH_3NHCl $Al(NO_3)_3$ $FeCl_3$	CH_3COOK HCOONa	CH_3COONH_4 NH_4CN

Section 7.5 Exercises

1 Write the equation for the reaction between each of the following combinations of acid and base.

- **a** Hydrochloric acid and potassium hydroxide
- **b** Methanoic acid and sodium hydroxide
- **c** Nitric acid and ammonia
- **d** Ethanoic acid and methylamine

2 For the combinations of acids and bases given in question **1a–c**, predict the pH of the salt solution formed when they react together fully.

3 Explain why the salt formed by the reaction of a strong acid with a weak base forms an aqueous solution with a pH that is less than 7.

4 Order the following salts from most acidic to least acidic when added to water:

NaCl, $MgSO_4$, $Al(NO_3)_3$, $KHCO_3$

5 Explain, using a chemical equation to assist your explanation, why iron(III) chloride forms an acidic solution when added to water, whereas sodium chloride does not.

6 Suggest a combination of an acid and a base that could produce a solution with pH:

- **a** equal to 7
- **b** below 7
- **c** above 7

7.6 INDICATORS

Many acids and bases and the products of their reaction are colourless solutions. There is often no obvious change in the solution when the reaction is complete. Most acid–base titrations therefore require an indicator to show when the neutralization reaction is complete. The point at which the reaction is complete is called the equivalence point. For example, in the titration of a hydrochloric acid solution with a sodium hydroxide solution, the equivalence point occurs when the amount (in mol) of NaOH that has been added is equal to the amount (in mol) of HCl that is present; that is, the mole ratio in the balanced equation is 1:1.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

AS 18.5.1 Describe qualitatively the action of an acid–base indicator. © IBO 2007

Natural indicators

The majority of acids are monoprotic, they only have one acidic hydrogen ion; however, there are a few acids that are polyprotic, but these will not be discussed in this course.

Acid–base indicators are usually weak acids, the dissociation of which can be represented as

$$\begin{array}{ll} \mathbf{HIn(aq) \rightleftharpoons H^+(aq) +} & \mathbf{In^-(aq)} \\ \textbf{colour 1} & \textbf{colour 2} \end{array}$$

The weak acid HIn is usually coloured and its conjugate base In^- is a distinctly different colour. Note that as a weak acid, the indicator dissociates, producing H^+ ions, and so could interfere with the reaction if large amounts of indicator were added. This is why we only add 3–4 drops of an indicator to the conical flask during a titration.

Figure 7.6.1 The acid–base indicator phenolphthalein is colourless in acidic solutions and a pink-purple colour in alkaline solutions, whereas methyl orange is red in acidic solutions and yellow in alkaline solutions.

When the pH of the solution containing the indicator changes, the position of equilibrium moves. A decrease in pH (increase in $[H^+]$) will push the equilibrium towards the left, making more HIn. The colour of the mixture of HIn and In^- will become closer to that of HIn (labelled above as colour 1). An increase in pH (decrease in $[H^+]$) will push the equilibrium towards the right, making more In^- and H^+. The colour will become closer to that of In^- (labelled above as colour 2).

Each indicator has a certain pH range for its colour change. Below that pH the indicator (and hence the solution it is in) has the colour of HIn (colour 1). Above that pH, the indicator has the colour of In^- (colour 2).

TABLE 7.6.1 ACID–BASE INDICATORS

Indicator	Colour of acidic form	pK_a (pK_{in})	pH range of colour change	Colour of basic form
Methyl orange	Red	3.7	3.1–4.4	Yellow
Bromophenol blue	Yellow	4.0	3.0–4.6	Blue
Bromocresol green	Yellow	4.7	3.8–5.4	Blue
Methyl red	Red	5.1	4.2–6.3	Yellow
Bromothymol blue	Yellow	7.0	6.0–7.6	Blue
Phenol red	Yellow	7.9	6.8–8.4	Red
Phenolphthalein	Colourless	9.3	8.3–10.0	Pink-purple

During a titration, the point at which the indicator changes colour is called the endpoint. An indicator for a titration is chosen so that the endpoint occurs as close as possible to the equivalence point. Choice of indicator therefore requires knowledge of the pH at the equivalence point of the titration. You will recall from section 7.5 that the pH at the equivalence point is determined by the combination of acid and base being titrated. The choice of indicator to suit the equivalence point will be discussed further on page 232.

The pH at which the indicator will change colour can be calculated using the pK_a of the indicator, also known as pK_{in}. Since the indicator is a weak acid, it has an acid dissociation constant, K_a or K_{in}.

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

$$K_{in} = \frac{[H^+][In^-]}{[HIn]}$$

To convert to pK_a, we take $-\log_{10}$ of all parts of this fraction.

$$-\log_{10}K_{in} = -\log_{10}[H^+]\frac{[In^-]}{[HIn]}$$

$$\text{so } pK_{in} = pH - \log_{10}\frac{[In^-]}{[HIn]}$$

$$\text{or } pH = pK_{in} + \log_{10}\frac{[In]}{[HIn]}$$

This equation is known as the **Henderson equation**.

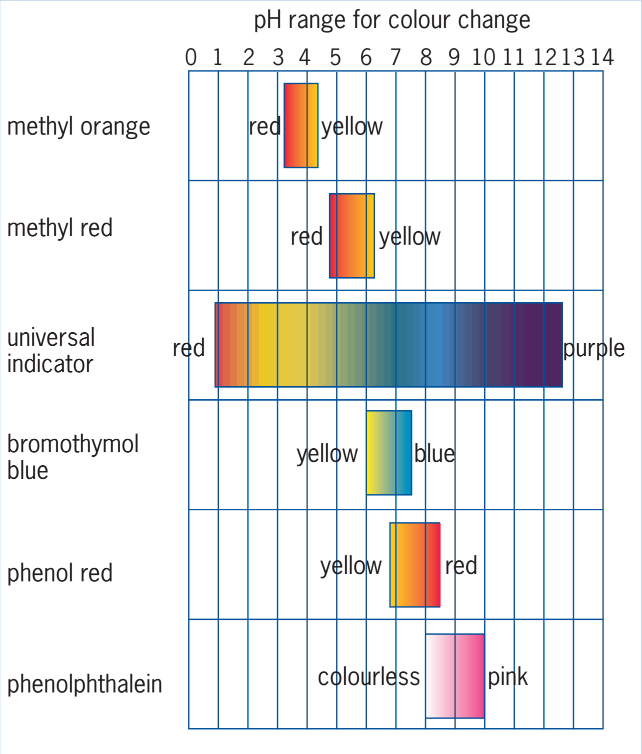


Figure 7.6.2 The colour change of indicators occurs over a specific pH range.

The colour of the indicator starts to change when $[In^-] = [HIn]$, and at this point the relationship simplifies to

$$pK_{in} = pH$$

The pH at the endpoint of the indicator is equal to the pK_a of the indicator, pK_{in}.

The range over which an indicator changes colour relates to the ability of the human eye to perceive that a colour change has occurred. In a mixture of two colours of about the same intensity, a ratio of more than 10:1 results in the eye seeing only the colour that is more concentrated, rather than a mixture of the two. So for an indicator that is red in acidic solutions (i.e. HIn is red) and yellow in more basic solutions (i.e. In^- is yellow):

$$\underset{\text{red}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\text{yellow}}{In(aq)}$$

if $\frac{[HIn]}{[In^-]} > 10$ the solution will appear red, with no hint of yellow and if $\frac{[HIn]}{[In^-]} < \frac{1}{10}$ the solution will appear yellow. Between these two limits the eye will see a range of orange colours.

The range of pH values between which the distinct colours are perceived can be calculated using the Henderson equation:

$$pH = pK_{in} - \log_{10}\frac{[HIn]}{[In^-]}$$

When $\frac{[\text{HIn}]}{[\text{In}^-]} = 10$, $\text{pH} = \text{p}K_{\text{in}} - \log_{10} 10$ and $\text{pH} = \text{p}K_{\text{in}} - 1$.

When $\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{1}{10}$, $\text{pH} = \text{p}K_{\text{in}} - \log_{10} 0.1$ and $\text{pH} = \text{p}K_{\text{in}} + 1$.

The expected colour change range for an indicator is therefore 2 pH units (one either side of the $\text{p}K_{\text{in}}$). This is an approximation based on the assumption of the 10 : 1 ratio for the perception of the colour and also assumes that both colours are equally intense.

CHEM COMPLEMENT

Plant indicators

Litmus indicator is a common acid–base indicator used in science classes. Although it is not commonly used for acid–base titrations, it is often used in testing solutions or gases for acidity. Litmus was first used as early as 1300 AD by Spanish alchemist Arnaldus de Villanova. It is a mixture of dyes extracted from plants called lichens, especially a purple dye called 'orcein' from the lichen *Roccella tinctoria*.

When litmus indicator is absorbed onto filter paper and dried, litmus paper is produced. Blue litmus paper turns red in acids and red litmus paper turns blue in bases. A solution can only be detected as neutral if it has been tested with both red and blue litmus paper and has not changed the colour of either. To test the pH of some gases (e.g. ammonia) wet litmus paper is used. The gas dissolves in the water and the solution reacts with the indicator. The presence of chlorine gas can also be tested with litmus paper, but the paper is bleached of its colour. This is not an acid–base reaction.

Many other plants can be used as acid–base indicators. Strongly coloured flowers can be ground up in the laboratory and their dye extracted with methylated spirits. Red cabbage can be used in a similar way to make an indicator.

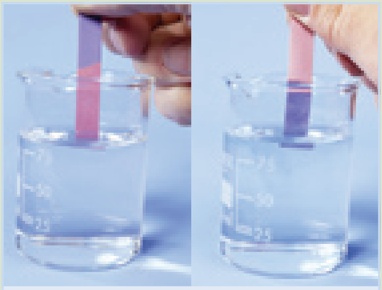


Figure 7.6.3 Blue litmus paper turns red in acids and red litmus paper turns blue in bases.

Figure 7.6.4 Many acid–base indicators are derived from plants, such as this red cabbage water indicator.

Choosing an indicator for a titration

AS 18.5.3 **Identify an appropriate indicator for a titration, given the equivalence point of the titration and the pH range of the indicator. © IBO 2007**

During a titration the ideal situation is for the indicator to change colour at a pH that is as close as possible to the pH of the equivalence point (in which equal amounts of acid and alkali have reacted). Ideally a small amount of alkali added will produce a dramatic colour change as the pH increases sharply and the indicator changes from its acidic form to its basic form. Knowledge of the nature of the acid and base involved in the titration allows prediction of the pH of the equivalence point, from the pH of the solution formed by the salt.

Consider the indicators described in table 7.6.1. Methyl orange changes colour from red to yellow in the pH range 3.1–4.4. This makes it suitable for the titration of a strong acid with a strong base (figure 7.6.5a) or of a strong acid with a weak base (figure 7.6.5c). Methyl red would also give good results for these titrations. Since the equivalence point of the titration of a strong acid with a strong base is at pH = 7, bromothymol blue would be a most suitable indicator for the titration. The titration of a weak acid with a strong base (figure 7.6.5b) would require an indicator with a colour change above 7. Either phenol red or phenolphthalein would also be suitable for this titration. Phenolphthalein is an indicator that is strongly favoured for titrations, as its colour change is very obvious—from colourless in its acidic form to a striking pink-purple colour in the basic form.

There are no indicators suitable for indicating the equivalence point for a titration of a weak acid with a weak base (figure 7.6.5d), as this titration curve does not have a vertical section with a width of 2 pH units, and there is no indicator that will change colour dramatically when a small volume of alkali is added. A pH meter is more suitable for plotting such titration curves and hence determining the equivalence point for the titration of a weak acid with weak base.

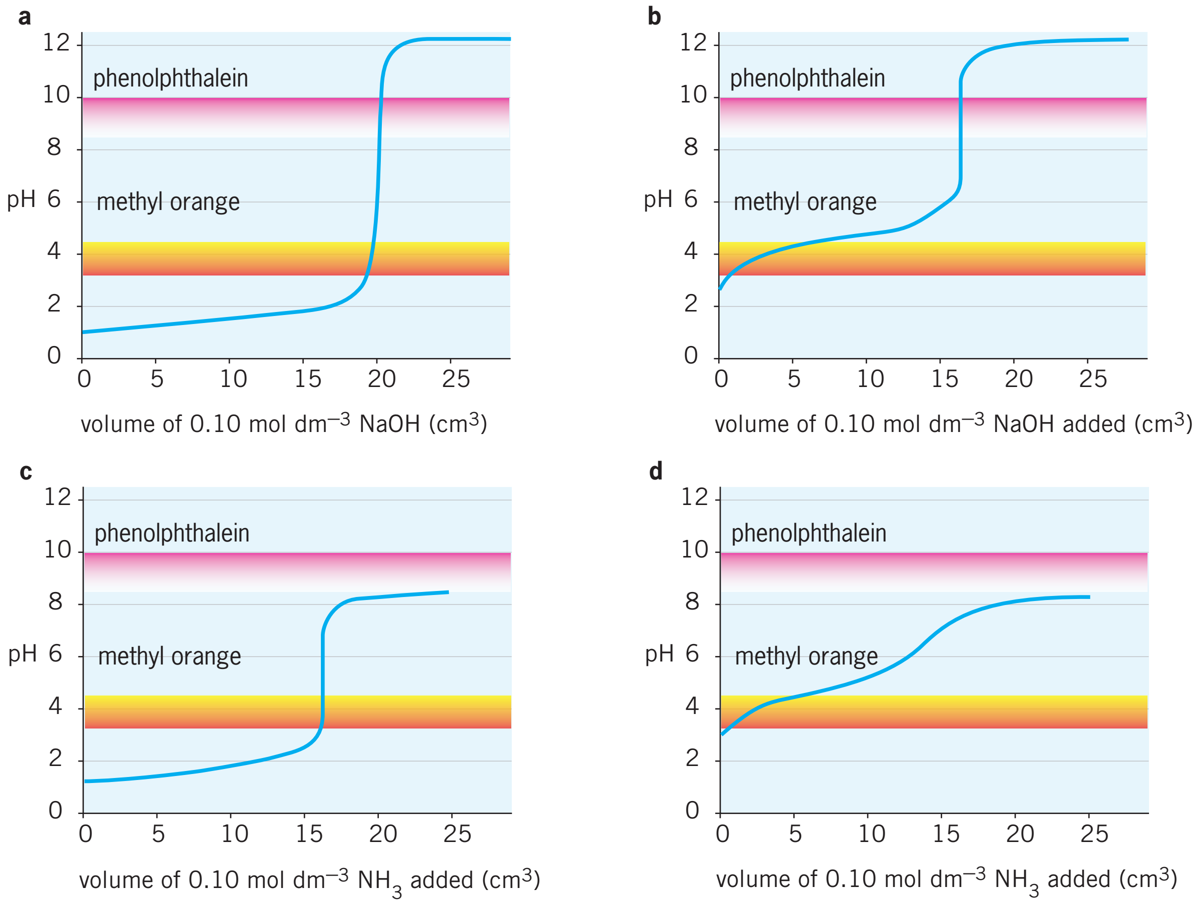


Figure 7.6.5 The titration curves for strong and weak acids with strong and weak bases, showing the pH ranges in which the indicators methyl orange and phenolphthalein change colour.

Figure 7.6.6 The reaction of sodium with water produces sodium hydroxide, which turns the phenolphthalein indicator in the water a stunning magenta (pink-purple) colour.

TABLE 7.6.2 SOME EXAMPLES OF ACID–BASE TITRATIONS AND THEIR APPROPRIATE INDICATORS

Acid	Base	pH of equivalence point	Suitable indicator	pH range of indicator	pK_{in}
HCl	NaOH	7	Methyl orange Bromothymol blue Phenolphthalein	3.1–4.4 6.0–7.6 8.3–10.0	3.7 7.0 9.3
CH_3COOH	NaOH	8.7	Phenolphthalein	8.3–10.0	9.3
HCl	NH_3	5.3	Methyl red	4.2–6.3	5.1

Section 7.6 Exercises

1 Distinguish between the terms *endpoint* and *equivalence point*.

2 Describe the features of a compound that enable it to act as an acid–base indicator.

3 The acid–base indicator bromocresol green is yellow in acidic solutions and blue in alkaline solutions. It has a pK_a of 4.7. State the colour of bromocresol green indicator in a solution with

- **a** pH = 3
- **b** pH = 4.7
- **c** pH = 9

4 Describe how the pK_a of an indicator compares with the pH range over which it changes colour.

5 Suggest an indicator that would change colour at the equivalence point for each of the following combinations of acid and base. (Hint: refer to your answer to question **2** of the section 7.5 exercises.)

a Hydrochloric acid and potassium hydroxide

b Methanoic acid and sodium hydroxide**c** Nitric acid and ammonia

d Ethanoic acid and methylamine

6 Explain why it is most suitable to use a pH meter to monitor the progress of the titration of a weak acid with a weak base.

7 Explain, using the Henderson equation, why the pH of an indicator solution in which $[HIn] = [In^-]$ is equal to pK_a of the indicator (pK_{in}).

8 A student is planning to perform a titration of ethanoic acid with sodium hydroxide. The student's choice of indicator is methyl orange. Explain whether or not this indicator will be suitable for the titration.

9 A student has added an unknown indicator to an acidic solution with pH = 5. The indicator could be bromophenol blue ($pK_a = 4.0$) or bromothymol blue ($pK_a = 7$). Explain how the student can determine which indicator has been used.

10 The indicator cresol red changes colour from yellow in acid solution to red in alkaline solution. The acid dissociation constant, K_a, for this indicator is 5.01×10^{-9} mol dm^{-3} and its hydrolysis can be represented as:

$$HCr(aq) + H_2O(l) \rightleftharpoons Cr^-(aq) + H_3O^+(aq)$$

Determine the magnitude of the ratio $\frac{[Cr^-]}{[HCr]}$ for cresol red and hence the colour of the indicator in solutions of pH:

a 4

b 13

c 8.3

Chapter 7 Summary

Terms and definitions

Acid dissociation constant, K_a A specialized equilibrium constant that is used to describe the dissociation of an acid in aqueous solution:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Acidic buffer solution A buffer solution that is made up of a weak acid and the salt of its conjugate base.

Back titration A measured excess of reagent is added to the sample being analysed. A reaction occurs completely and usually quickly, and the amount of unreacted reagent in the solution is then determined by direct titration.

Base dissociation constant, K_b A specialized equilibrium constant that is used to describe the dissociation of a base in aqueous solution:

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Basic buffer solution A buffer solution that is made up of a weak base and the salt of its conjugate acid.

Buffer region The nearly horizontal region of a titration curve which is made up of a mixture of the acid or base being titrated and the salt that has been formed.

Buffer solution A solution containing a mixture of solutes that resists changes in pH when a small amount of an acid or a base is added.

Concordant Results which fall within the range of the systematic error of the equipment being used. In particular this is applied to volumes of solution delivered from a burette during a titration.

Endpoint The point in the titration (pH) at which the indicator changes colour.

Equivalence point The point in the titration (pH) at which the acid or base has been completely neutralized, i.e. the acid and the base have reacted in the correct stoichiometric ratio.

Half neutralized The stage of the titration when exactly half of the acid or base being titrated has been neutralized. At this stage pH = pK_a or pOH = pK_b.

Henderson equation: $\text{pH} = \text{p}K_{in} + \log_{10}\frac{[In^-]}{[HIn]}$

The equation used to calculate the pH of an indicator.

Ionic product constant (ionization constant) of water, K_w A specialized equilibrium constant used to describe the acid–base reaction of water molecules in aqueous solution:

$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ at 25°C.

pK_a This is equal to $-\log_{10}K_a$ (see acid dissociation constant).

pK_b This is equal to $-\log_{10}K_b$ (see base dissociation constant).

pOH This is equal to $-\log_{10}[OH^-]$. It is a quantity which gives an idea of the strength of a base.

Salt hydrolysis The reaction of a salt with water.

Titration curve A graph of pH against volume for a titration of an acid with a base (or a base with an acid).

Concepts

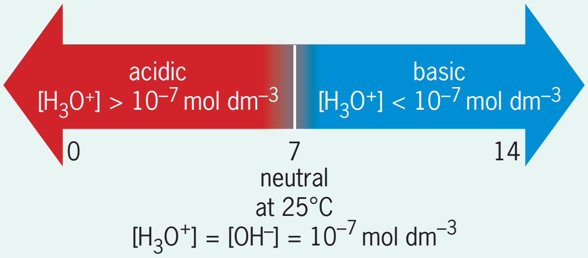
- Water undergoes self-ionization, according to:

  $$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

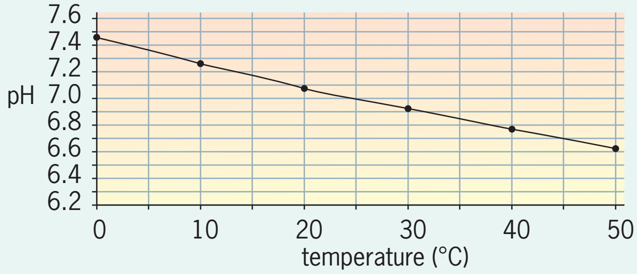
- The pH scale is based on the ionic product constant of water (K_w), where:

  $$K_w = [H_3O^+][OH^-] = 10^{-14}\ \text{mol}^{-2}\ \text{dm}^{-6} \text{ at } 25°C$$

- pH is a logarithmic scale measuring the concentration of hydronium ions, where pH = $-\log_{10}[H_3O^+]$.

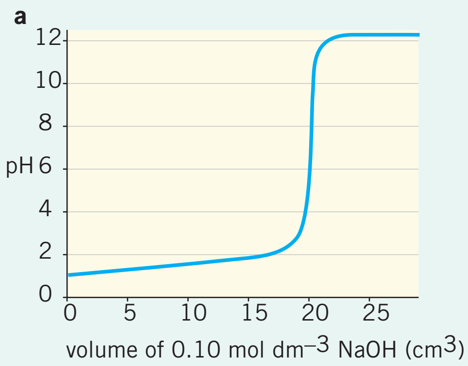


- For alkaline solutions, pOH measures the concentration of hydroxide ions where pOH = $-\log_{10}[OH^-]$.
- Pure water is neutral at all temperatures, but pH varies with temperature.

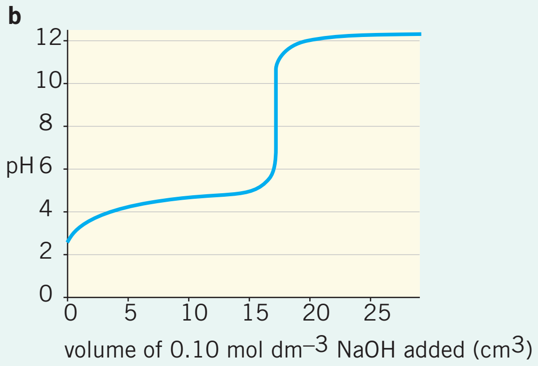


- An acid dissociation constant, K_a can be used to carry out calculations involving the concentration of a weak acid or its conjugate base or the pH of the solution. In these calculations, we make the important simplification that $[HA]_{eq} \cong [HA]_i$:
  $$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$
- A base dissociation constant, K_b, can be used to carry out calculations involving the concentration of a weak base or its conjugate acid or the pH of the solution. In these calculations, we make the important simplification that $[B]_{eq} \cong [B]_i$
  $$K_b = \frac{[HB^+][OH^-]}{[B]}$$
- The strength of an acid or a base can be determined from its K_a or K_b. The greater the K_a, the stronger the acid, and the greater the K_b, the stronger the base. The smaller the pK_a, the stronger the acid, the smaller the pK_b, the stronger the base.
- Buffers are solutions that resist change in pH on the addition of a small amount of acid or base. They may be made up of a weak acid and its conjugate base or a weak base and its conjugate acid.
- The pH of a buffer can be determined by the equation $pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$.
- An acid is half neutralized when the amount of base that has been added is equal to half of the original amount of acid present.
- Hydrolysis reactions of salts produce solutions with varying pH:
  - Strong acid–strong base gives a neutral salt.
  - Strong acid–weak base gives an acidic salt.
  - Weak acid–strong base gives a basic salt.
  - Weak acid–weak base could have acidic, neutral or basic pH.
- Acid–base indicators consist of a weak acid, HIn and its conjugate base In^-, at least one of which must be intensely coloured. The titration endpoint occurs when the pH of solution equals the pK_a of the indicator.
- An appropriate indicator for an acid–base reaction has its pK_a in the vertical section of the titration curve for that reaction.
- Titration curves (below) have a characteristic shape, depending on the combination of strong and weak acid and base.

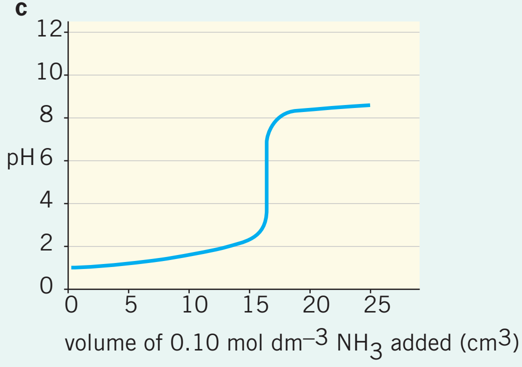
Strong acid and strong base



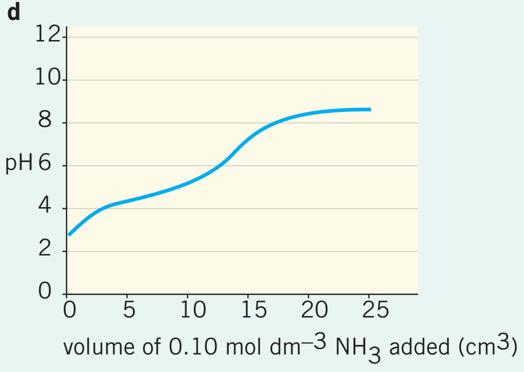
Weak acid and strong base



Strong acid and weak base



Weak acid and weak base



Chapter 7 Review questions

1 Determine the pH of the following solutions.

a [HCl] = 0.0010 mol dm^{-3}

b [H_2SO_4] = 5.83 × 10^{-3} mol dm^{-3}

c [NaOH] = 8.52 × 10^{-6} mol dm^{-3}

d [$Sr(OH)_2$] = 7.73 × 10^{-9} mol dm^{-3}

2 Calculate the [H_3O^+] for solutions where:

a pH = 2.25

b pH = –1

3 250 cm^3 of 10.0 mol dm^{-3} nitric acid is diluted to 3.00 dm^3 with distilled water. Determine the pH of the resultant solution.

4 9.35 g of solid NaOH is carefully dissolved in 400 cm^3 of water. Calculate the pH of the resultant solution.

5 Deduce the volume of water that would need to be added to 5.0 cm^3 of 14.0 mol dm^{-3} nitric acid to change the resulting solution to a pH of 2.00.

6 Write the acid dissociation constant expression for each of the following monoprotic acids.

a Hydrocyanic acid (HCN)

b Propanoic acid (CH_3CH_2COOH)

c Nitrous acid (HNO_2)

7 Phenol, also known as carbolic acid, was one of the first antiseptic agents used in surgery to help prevent infection. A weak organic acid of chemical formula C_6H_5OH, it has an acid dissociation constant of 1.05 × 10^{-10} mol dm^{-3}. Calculate the pH of a 3.5 × 10^{-3} mol dm^{-3} solution of phenol, given the equation for its reaction with water:

$$C_6H_5OH(aq) + H_2O(l) \rightleftharpoons C_6H_5O^-(aq) + H_3O^+(aq)$$

8 The food preservative sodium benzoate is derived from benzoic acid, a weak monoprotic acid that has a pK_a of 4.20. Calculate the pH of a 0.020 mol dm^{-3} solution of benzoic acid, given the equation for its hydrolysis is:

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(aq)$$

9 The pH of a 0.050 mol dm^{-3} solution of nitrous acid is measured as 2.22. Determine the acid dissociation constant for nitrous acid, given that the equation for its hydrolysis is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$$

10 The pK_b of ethylamine is 3.27.

a Determine the equation for the dissociation of ethylamine, $CH_3CH_2NH_2$, in water.

b State the expression for the base dissociation constant, K_b, for ethylamine

c Deduce the value for the acid dissociation constant, K_a, for the conjugate acid of ethylamine at 298 K.

11 The conjugate base of butanoic acid is the butanoate ion, $CH_3(CH_2)_2COO^-$. At 25°C, pK_b of butanoic acid is 9.18.

a Determine the equation for the dissociation of the butanoate ion in water.

b State the expression for the base dissociation constant, K_b, of the butanoate ion.

c Calculate the pH of a 0.050 mol dm^{-3} solution of butanoic acid.

12 During a titration of ethanoic acid with sodium hydroxide, the solution formed when ethanoic acid is exactly half neutralized can act as a buffer solution

a Explain what is meant by the term *half neutralized*

b The pK_a of ethanoic acid is 4.76. Calculate the value of [H^+] in this buffer solution, showing your working.

c Write an equation to show the buffer action of this solution when a small amount of base is added.

13 **a** Identify two substances that can be added to water to form a basic buffer solution.

b Using an equation to support your explanation, describe what happens when a small amount of acid solution is added to the buffer solution prepared in part **a**.

14 Explain why a mixture of 50 cm^3 of 0.10 mol dm^{-3} hydrochloric acid solution and 50 cm^3 of 0.20 mol dm^{-3} ammonia solution can act as a buffer solution, and calculate the pH of this buffer solution at 25°C (pK_b(NH_3) at 25°C = 4.75).

15 For each of the following titrations identify:

i the species present at the equivalence point

ii the pH of the reaction mixture at the equivalence point (7, above 7, below 7)

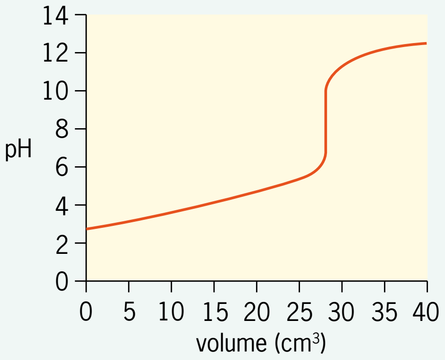
iii an appropriate indicator.

a The titration of an NaOH solution with an HNO_3 solution

b The titration of an NH_3 solution with an HCl solution

c The titration of a KOH solution with a CH_3COOH solution

16 Consider the graph of pH against volume shown below.



a From the shape of the graph, suggest a possible identity for the two solutions being reacted in this titration.

b Use the graph to determine the pH of the acid solution.

c Use the graph to determine the volume of the alkali that is added in order to reach the equivalence point of the titration.

d State the pH of the solution at the equivalence point.

e Identify an indicator that could be used to detect the equivalence point of this titration.

17 Hydrogen sulfide (H_2S) can act as a weak acid in aqueous solution.

a Write an equation for the ionization of hydrogen sulfide in water.

b 3.4 g of hydrogen sulfide will dissolve in 1.0 dm^3 of water at room temperature to form a saturated solution. Calculate the concentration of this solution.

c Given that the K_a for hydrogen sulfide is 9.88×10^{-8} mol dm^{-3}, calculate the pH of the saturated solution.

d Addition of solid sodium hydrogensulfide (NaHS) to the saturated solution will form a buffer solution.

i Describe the function of a buffer solution.

ii Using Le Chatelier's principle, explain what happens in this buffer solution when a small amount of HCl is added.

18 The formula HIn is used to represent a general indicator that is a weak acid.

a Write the equation for the dissociation of HIn in aqueous solution.

b Explain why an indicator changes colour during a titration.

19 Methyl orange is a common acid–base indicator that changes from a pink-red colour to yellow over a small range of pH values. The reaction of methyl orange and its conjugate may be represented as:

$$HMe(aq) + H_2O(l) \rightleftharpoons Me^-(aq) + H_3O^+(aq)$$
$$K_a = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$$

a Write an expression for the acidity constant of methyl orange.

b Determine the pH of the endpoint for this indicator.

20 Phenol red ($pK_a = 7.9$) is an acid–base indicator that changes from yellow to red.

The reaction may be represented as:

$$HIn(aq) + H_2O(l) \rightleftharpoons In^-(aq) + H_3O^+(aq)$$

The $In^-(aq)$ form of the indicator is red.

a State the colour that the indicator will exhibit in acid solution.

b State the lowest pH of a solution that you would expect to appear a strong red colour.

Web Destinations

www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 7 Test

Part A: Multiple-choice questions

1 Which mixture would produce a buffer solution when dissolved in 1.0 dm^3 of water?

A 0.30 mol of $NH_3(aq)$ and 0.30 mol of $HCl(aq)$

B 0.30 mol of $NH_3(aq)$ and 0.15 mol of $HCl(aq)$

C 0.30 mol of $NH_3(aq)$ and 0.60 mol of $HCl(aq)$

D 0.30 mol of $NH_3(aq)$ and 0.15 mol of $H_2SO_4(aq)$

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2 The pK_a values of four acids are as follows.

W 4.87
X 4.82
Y 4.86
Z 4.85

What is the correct order when these acids are arranged in order of **increasing** acid strength?

A X, Z, Y, W

B X, Y, Z, W

C W, Z, Y, X

D W, Y, Z, X

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3 Ammonia (NH_3) is a weak base in aqueous solution with an ionization constant K_b. What expression is equal to the ionization constant for the following reaction?

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

A $\frac{K_w}{K_a}$ **B** $\frac{K_a}{K_w}$

C $\frac{K_w}{K_b}$ **D** $\frac{K_b}{K_w}$

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4 A base of concentration 0.10 mol dm^{-3} is titrated with 25 cm^3 of an acid of concentration 0.10 mol dm^{-3}. Which base–acid pair would have the highest pH at the equivalence point?

A $NaOH(aq)$ and $CH_3COOH(aq)$

B $NaOH(aq)$ and $HNO_3(aq)$

C $NH_3(aq)$ and $HNO_3(aq)$

D $NH_3(aq)$ and $CH_3COOH(aq)$

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5 Which solution has the lowest pH value?

A Aluminium sulfate

B Sodium nitrate

C Potassium chloride

D Sodium ethanoate

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6 Which neutralization reaction could use phenolphthalein (pK_a = 9.3) and not methyl orange (pK_a = 3.7) as an indicator?

A $NaOH(aq)$ and $HNO_3(aq)$

B $NH_3(aq)$ and $CH_3COOH(aq)$

C $NaOH(aq)$ and $CH_3COOH(aq)$

D $NH_3(aq)$ and $HNO_3(aq)$

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7 Water dissociates according to the equation

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \Delta H = +56 \text{ kJ}$$

At 25°C water has a pH of 7. Which of the following occurs when water is heated to 30°C?

A It remains neutral and its pH decreases.

B It becomes acidic and its pH decreases.

C It remains neutral and its pH increases.

D It becomes acidic and its pH increases.

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8 The strengths of organic acids can be compared using K_a and pK_a values. Which acid is the strongest?

A Acid A pK_a = 6

B Acid B pK_a = 3

C Acid C $K_a = 1 \times 10^{-5}$

D Acid D $K_a = 1 \times 10^{-4}$

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9 Which is the correct statement about the pH and pOH values of an aqueous solution at 25°C?

A pH + pOH = 14.0

B $\text{pH} + \text{pOH} = 1.0 \times 10^{-14}$

C pH × pOH = 14.0

D $\text{pH} \times \text{pOH} = 1.0 \times 10^{-14}$

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10 Which compound will dissolve in water to give a solution with a pH greater than 7?

- **A** Sodium chloride
- **B** Potassium carbonate
- **C** Ammonium nitrate
- **D** Lithium sulfate

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(10 marks)

Web Destinations www.pearsoned.com.au/schools

For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 The indicator bromophenol blue, HIn(aq), has a form that is yellow and an $In^-(aq)$ form that is blue.

a Write an equation to show how bromophenol blue acts as an indicator.

(1 mark)

b State and explain the colour of bromophenol blue:

i on the addition of a strong acid.

ii at the equivalence point of a titration.

(3 marks)

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2 **a** Calculate the K_a value of methanoic acid, HCOOH, using Appendix 5.

(1 mark)

b Based on its K_a value, state and explain whether methanoic acid is a strong or weak acid.

(2 marks)

c Calculate the hydrogen ion concentration and the pH of a 0.010 mol dm^{-3} methanoic acid solution. State one assumption made in arriving at your answer.

(4 marks)

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3 A buffer solution can be made by dissolving 0.25 g of sodium ethanoate in 200 cm^3 of 0.10 mol dm^{-3} ethanoic acid. Assume that the change in volume is negligible.

a Define the term *buffer solution*.

(2 marks)

b Calculate the concentration of the sodium ethanoate in mol dm^{-3}.

(3 marks)

c Calculate the pH of the resulting buffer solution by using information from Appendix 5.

(3 marks)

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Part C: Data-based question

The following table is to be used as appropriate in answering this question.

Solution	Solute	Conc / mol dm^{-3}	*K* / mol dm^{-3}
A	HCl(aq)	0.25	
B	$CH_3COOH(aq)$	0.25	$K_a = 1.74 \times 10^{-5}$
C	NaOH(aq)	0.25	
D	$NH_3(aq)$	0.25	$K_b = 1.78 \times 10^{-5}$
E	$CH_3COONa(aq)$	0.25	

a Calculate the pH of solution A **and** indicate why no K_a value is given for this solution.

(2 marks)

b Calculate the pH of solution B. State any assumptions made.

(4 marks)

c Solutions B and C can be mixed to form a buffer solution.

i Describe the purpose of a buffer solution.

ii Give the relative amounts of solution B and C to form a buffer solution and outline your reasoning. **[No calculations necessary.]**

(3 marks)

d Determine the pK_b of solution D.

(1 mark)

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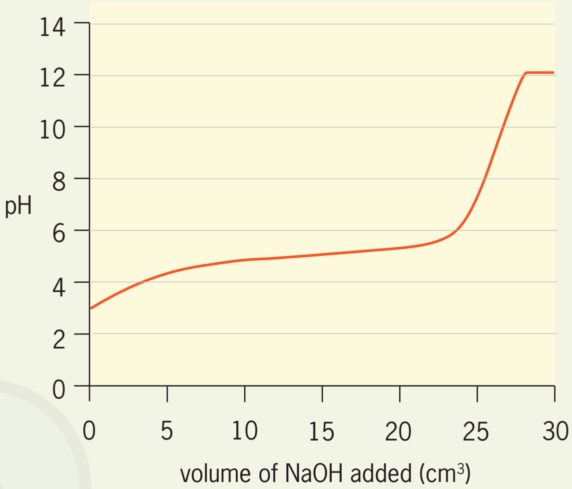
Part D: Extended-response question

Benzoic acid is a weak *monoprotic* acid.

a The experimentally determined graph below shows the change in pH when 0.10 mol dm^{-3} aqueous sodium hydroxide is added to 25 cm^3 of 0.10 mol dm^{-3} aqueous benzoic acid.



i Calculate the pH when the benzoic acid is half neutralized and explain how you arrived at your answer.

(2 marks)

ii Explain by reference to Appendix 5 why phenolphthalein is a suitable indicator for this titration.

(2 marks)

b The experiment was repeated using 25 cm^3 of 0.10 mol dm^{-3} hydrochloric acid.

i Sketch the graph you would expect from the results of this second experiment.

(3 marks)

ii State and explain any similarities and differences between the two graphs.

(4 marks)

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Total marks: 50

8

OXIDATION AND REDUCTION

Chapter overview

This chapter covers the IB Chemistry syllabus Topic 19: Oxidation and Reduction.

By the end of this chapter, you should be able to:

- describe the standard hydrogen half-cell
- define the term standard electrode potential, $E^\ominus$
- use the table of standard electrode potentials to calculate cell potentials
- use the table of standard electrode potentials to predict whether a reaction will be spontaneous
- describe and explain the processes occurring during the electrolysis of an aqueous solution
- predict the products of the electrolysis of an aqueous solution
- determine the relative amounts of products formed during electrolysis by considering the factors that may change these amounts
- describe the process of electroplating.

IBO Assessment statements 19.1.1 to 19.2.3

Sources of portable electricity generation, commonly known as batteries (but known to chemists as voltaic cells), have become a fundamental part of modern life. Mobile phones, laptop computers and digital cameras are voracious users of voltaic cells, and the development of electric cars in the near future is largely dependent on further progress in voltaic cell technology. The voltaic cell has changed greatly since the earliest voltaic cells, such as the Daniell cell, in which the difference in reactivity between copper and zinc was used to generate electricity.

Figure 8.0.1 A Daniell cell is made up of a copper electrode (often a copper container) with a porous partition separating the copper sulfate solution from the zinc sulfate solution. A zinc anode is in the centre of the cell.

Figure 8.0.2 The viability of electric cars is largely dependent on the efficiency of their rechargeable batteries.

8.1 STANDARD ELECTRODE POTENTIALS

In Standard Level Chemistry we studied redox reactions and the production of electricity in a voltaic cell. Half-cells were made up of a metal in an aqueous solution of its cation, such as copper metal in a solution of copper sulfate, and these were joined by an external circuit and a salt bridge.

QuickTime Video
Voltaic cells: the copper–zinc cell

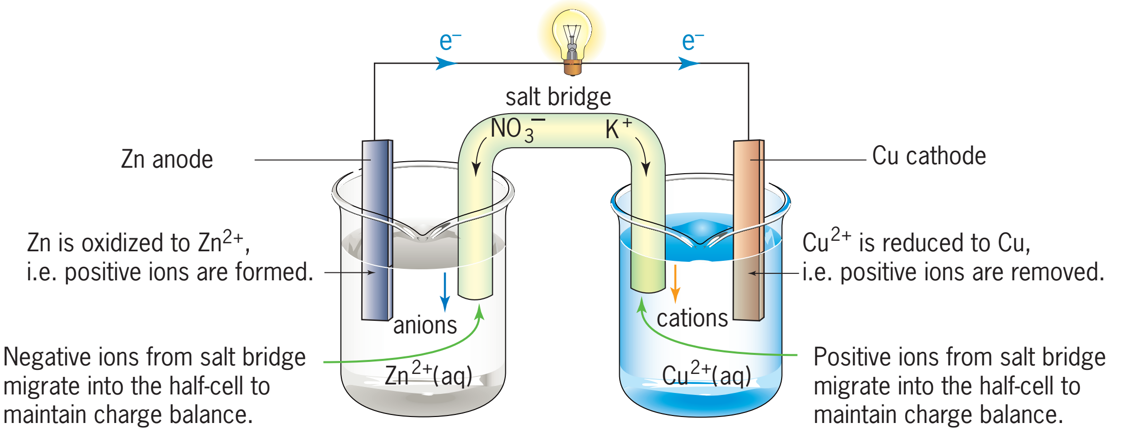

Figure 8.1.1 A voltaic cell is made up of two half-cells joined by an external circuit and a salt bridge.

Experimentally, the voltage generated by any voltaic cell can be measured by connecting a voltmeter to the external circuit (see figure 8.0.1). The voltage of a voltaic cell is determined by the difference in reactivity of the metals (or non-metals) that are connected together. The greater the difference in reactivity, the greater the voltage will be. To predict the voltage generated by a pair of half-cells, an electrochemical series must be consulted. Such a series is put together by comparing the strength of the metal as a reducing agent to that of hydrogen gas. This convention places the $H_2(g)/H^+(aq)$ half-cell in the middle of the series of what is known as standard electrode potentials (see figure 8.1.7).

CHEM COMPLEMENT

Why hydrogen?

Hydrogen is a gas that reacts explosively with oxygen. It has the lowest density of all gases and escapes easily from less than well-sealed vessels. Hydrogen does not dissolve in water. It is a difficult gas to work with. So why would $H_2(g)/H^+(aq)$ be used as a standard to which other half-cells are compared?

Historically, the ability of metals to withstand attack by acids, $H^+(aq)$, has been important. Those metals that did not react with acids, such as copper, mercury, silver and gold, were known as noble metals. The strength of an oxidizing agent could be compared to acids; if it did not react with copper, then it was not as strong an oxidizing agent as the hydrogen ion. This appears to be the source of the choice of the $H_2(g)/H^+(aq)$ half-cell as that with an electrode potential of 0.00 V. It is convenient that it appears approximately half way down a list of standard electrode potentials, but it is unlikely that convenience alone was the reason for this choice, which is now simply taken as convention.

AS 19.1.1
Describe the standard hydrogen electrode.
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A **standard hydrogen electrode** (also be known as the **standard hydrogen half-cell**) is a half-cell made up of an acidic solution (containing $H^+(aq)$) with a glass tube dipping in the solution through which hydrogen gas is bubbled. A platinum electrode is contained within the glass tube, so is in contact with both the $H^+(aq)$ and $H_2(g)$. The surface of the electrode is covered with platinum black, a fine powder of platinum with a high surface area. The coating of platinum black serves an important function as a catalyst for the reaction occurring at the electrode. Like other standard measurements, the concentration of the solution must be 1.00 mol dm^{-3}, the pressure of the gas 1.01×10^2 kPa and the temperature at which these are measured should be 298 K.

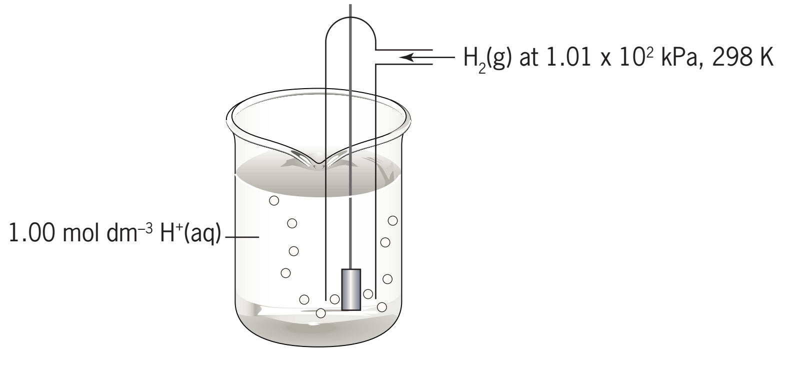

Figure 8.1.2 The standard hydrogen electrode is made up of a 1.00 mol dm^{-3} solution of $H^+(aq)$, together with hydrogen gas at a pressure of 1.01×10^2 kPa at 298 K.

The standard hydrogen electrode has a standard electrode potential, $E^\ominus$ of 0.00 V. The half-equation that occurs in the standard hydrogen electrode is

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

The double arrow in this equation means that the reaction is reversible. The direction in which the reaction goes will depend on the half-cell to which the standard hydrogen electrode is connected. The hydrogen ion, H^+, is an oxidizing agent and hydrogen gas, H_2, is a reducing agent. Hydrogen ions can oxidize any reducing agent with a negative $E^\ominus$ value, while hydrogen gas can reduce any oxidizing agent with a positive $E^\ominus$ value.

AS 19.1.2
Define the term *standard electrode potential* ($E^\ominus$).
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Video
Voltaic cells: the zinc–hydrogen cell

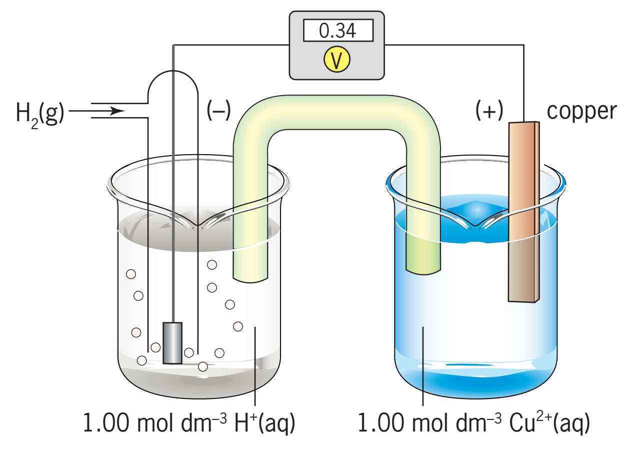

Figure 8.1.3 Measuring the standard electrode potential of copper.

The term **standard electrode potential** refers to the voltage or potential of a particular half-cell when it is connected to the standard hydrogen half-cell. This connection is by means of an external circuit as well as a salt bridge.

QuickTime CW Video
Standard electrode potentials

To measure the standard electrode potential of a Cu/Cu^{2+} half-cell, the two half-cells would be arranged as shown in figure 8.1.3.

To maintain **standard conditions**, the concentration of $Cu^{2+}(aq)$ must be 1.00 mol dm^{-3} and the temperature of the solution should be 298 K. Under these conditions, the cell voltage is 0.34 V, with the hydrogen electrode connected to the negative (black) terminal of the voltmeter and the copper half-cell connected to the positive (red) terminal of the voltmeter. This makes the standard electrode potential of copper +0.34 V, since it is positive in comparison to the standard hydrogen electrode.

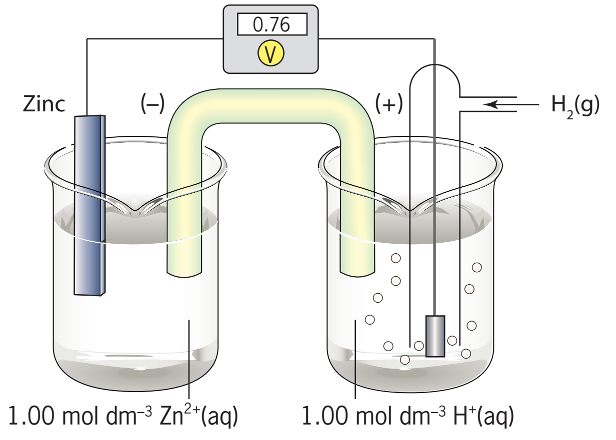

Figure 8.1.4 Measuring the standard electrode potential of zinc.

The standard electrode potential of all half-cells may be measured in this manner. When a zinc half-cell is connected to the standard hydrogen electrode (figure 8.1.4), the voltmeter will only give a positive reading when the zinc electrode is connected to the negative (black) terminal of the voltmeter and the standard hydrogen electrode is connected to the positive (red) terminal. This means that the standard electrode potential of zinc is –0.76 V.

Not all half-cells consist of a metal electrode in a solution of the metal ions, such as the Zn/Zn^{2+} and Cu/Cu^{2+} half-cells. Half-cells can also be made up of non-metals and of transition metal ions in different oxidation states. In these cases the electrode is made of an inert material such as graphite or platinum.

This electrode does not take part in the reaction, but conducts electricity to the **electrolyte** and may, in the case of a platinum electrode, catalyse the reaction. If the non-metal is a gas, then it may be delivered through a tube, in the same way that hydrogen is introduced into the standard hydrogen half-cell. Otherwise, the non-metal may be sufficiently soluble in water to produce a solution with a concentration of 1.00 mol dm^{-3}. If the oxidizing agent and reducing agent are both transition metal ions, e.g. Fe^{2+}/Fe^{3+}, the electrode will be inert and both ions will be in solution.

Figure 8.1.5 The standard electrode potential of the Fe^{2+}/Fe^{3+} half-cell can be measured using this apparatus in which the standard hydrogen electrode is in the small inner tube. Both half-cells have a platinum electrode.

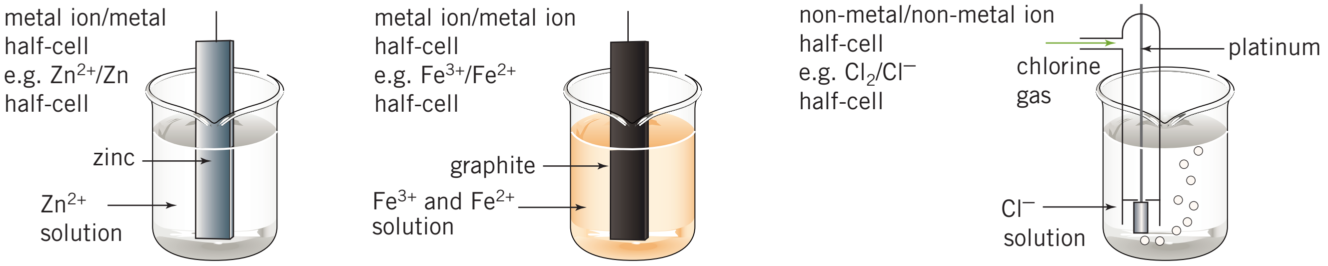

Figure 8.1.6 Some half-cells have inert electrodes, while the electrodes of other half-cells are reducing agents.

Calculating cell potentials

AS 19.1.3
Calculate cell potentials using standard electrode potentials. © IBO 2007

The **cell potential** is equal to the difference between the electrode potentials of the two half-cells of which the cell is composed. If one of the two half-cells is the standard hydrogen half-cell, then the cell potential is equal to the electrode potential of the other half-cell. For example, the voltage (or cell potential) of the cell made up of the standard hydrogen half-cell and the Cu/Cu^{2+} half-cell can be measured as 0.34 V. Therefore, if the $E^\ominus$ of the standard hydrogen half-cell is set as 0.00 V, the $E^\ominus$ of the Cu/Cu^{2+} half-cell will be +0.34 V.

A table of standard electrode potentials can be used to find the cell potential of any combination of half-cells. The standard electrode potentials ($E^\ominus$) have been found for all half-cells by connecting them to the standard hydrogen half-cell and measuring the cell potential. These may be found in figure 8.1.7 or in table 14 of the IB Data booklet © IBO 2007.

The table of standard electrode potentials shows all half-equations as reversible reactions. The species on the left-hand side of the series are all oxidizing agents, and those on the right-hand side are reducing agents. (**R**educing agents on the **R**ight.) The strongest oxidizing agent is found at the bottom left-hand corner and oxidizing agent strength decreases up the series. Fluorine gas is the strongest oxidizing agent. The voltaic cell constructed from the standard fluorine half-cell and the standard hydrogen half-cell has a potential difference of 2.87 V. Fluorine, the most electronegative element, has a strong tendency to accept electrons (be reduced). Just as fluorine gas, F_2, is a powerful oxidizing agent, its conjugate, the fluoride ion, F^-, is a very weak reducing agent. The fluoride ion has a filled valence shell of eight electrons and has very little tendency to give away electrons (be oxidized).

At the top of the table of standard electrode potentials is the half-equation for the reduction of the lithium ion, Li^+. Li^+ is the weakest oxidizing agent as it has the least tendency to accept electrons. Conversely, lithium metal is the strongest reducing agent, the potential difference between standard lithium and hydrogen half-cells being 3.03 V. In summary, oxidizing agent strength increases down the left-hand side of the electrochemical series and reducing agent strength increases up the right-hand side of the series.

oxidizing strength increases

reducing strength increases

Oxidized species	$\rightleftharpoons$	Reduced species	$E^{\ominus}$ volts
$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	–3.03
$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$	–2.92
$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$	–2.87
$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.36
$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.66
$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$	–1.18
$H_2O(l) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	–0.44
$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$	–0.23
$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$	–0.13
$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^-$	$\rightleftharpoons$	$Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq)$	+0.40
$Cu^+(aq) + e^-$	$\rightleftharpoons$	$Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	$I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^-$	$\rightleftharpoons$	$Br^-(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^-$	$\rightleftharpoons$	$F^-(aq)$	+2.87

Figure 8.1.7 The table of standard electrode potentials has the strongest reducing agent at the top right-hand side and the strongest oxidizing agent at the bottom left-hand side.

The cell potential is equal to the amount of energy delivered to electrons in a voltaic cell under standard conditions and may also be known as the **electromotive force**, **emf**, of the cell. If standard conditions of temperature, pressure and concentration are employed, the symbol $\boldsymbol{E^{\ominus}_{\text{cell}}}$ is used to show the magnitude of the **potential difference** between the oxidizing agent and the reducing agent (which is also the cell potential or emf). The unit of potential difference is the volt, V.

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}}$$

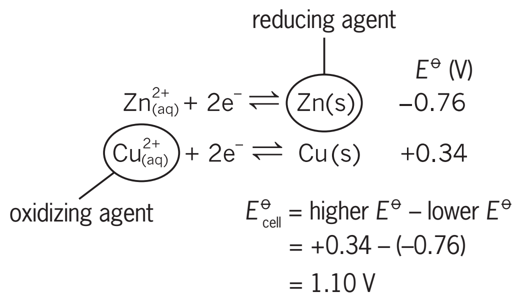

Figure 8.1.8 Remembering how to find the potential difference of a voltaic cell.

The half-cell with the oxidizing agent in it will be the one with the more positive standard electrode potential, $E^{\ominus}$. Note that it may not be positive, but will be more positive than the $E^{\ominus}$ of the cell with the reducing agent in it.

The cell potential for a standard Cu^{2+}/Cu half-cell connected to the standard Zn^{2+}/Zn half-cell can be calculated as follows:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\ V$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\ V$$

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}} \\ &= 0.34 - (-0.76) = 0.34 + 0.76 = 1.10\ V \end{aligned}$$

Worked example 1

a Write the overall ionic equation and calculate the cell potential when standard half-cells containing Cl^-/Cl_2 and I^-/I_2 are coupled in a voltaic cell.

b Write the overall ionic equation and calculate the cell potential when standard half-cells containing Mg/Mg^{2+} and Fe/Fe^{2+} are coupled in a voltaic cell.

Solution

a The standard electrode potentials for these two half-cells are:

$$\tfrac{1}{2}I_2(s) + e^- \rightleftharpoons I^-(aq) \qquad E^{\ominus} = +0.54\ V$$
$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^{\ominus} = +1.36\ V$$

Cl_2 is the stronger oxidizing agent (has the more positive $E^{\ominus}$).

So $\tfrac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-(aq)$

I^- is oxidized to $\tfrac{1}{2}I_2$ by the chlorine gas, so:

$$I^-(aq) \rightarrow \tfrac{1}{2}I_2(g) + e^-$$

Thus, the overall equation is:

$$\tfrac{1}{2}Cl_2(g) + I^-(aq) \rightarrow Cl^-(aq) + \tfrac{1}{2}I_2(s)$$

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}} \\ &= 1.36 - 0.54 = 0.82\ V \end{aligned}$$

b The standard electrode potentials for these two half-cells are:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^{\ominus} = -2.36\ V$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^{\ominus} = -0.44\ V$$

Fe^{2+} is the stronger oxidizing agent (has the more positive $E^{\ominus}$)

So $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

Mg is oxidized to Mg^{2+} by the Fe^{2+} ions, so:

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$$

Thus, the overall equation is:

$$Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$$

$$\begin{aligned} E^{\ominus}_{cell} &= E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}} \\ &= -0.44 - (-2.36) = 1.92\ V \end{aligned}$$

The cell potential for a spontaneous reaction must always have a positive value.

Predicting whether a reaction will be spontaneous

A table of standard electrode potentials allows the prediction of whether a redox reaction between two species will occur. To determine whether or not a spontaneous redox reaction will occur, we use the following steps:

Step 1: Write out the equations, one below the other, in order of standard electrode potential with the equation having the least positive standard electrode potential at the top (i.e. in the order in which they are found in figure 8.1.7). You may need to refer to figure 8.1.7 for the equations, or they may be given to you.

Step 2: Identify all possible reactants by highlighting them in the list you have written out. One reactant must be oxidized, while the other is reduced. This will only be possible if you have highlighted reactants on opposite sides of the series.

Step 3: The strongest oxidizing agent will undergo reduction. For this reason, the highlighted oxidizing agent must have a more positive $E^\ominus$ value (be lower on the left-hand side of the series) than the highlighted reducing agent (which will be on the right-hand side). Visually, a line joining the oxidizing agent and the reducing agent should diagonally cross the table going 'uphill' from left to right, or from a more positive $E^\ominus$ value to a more negative $E^\ominus$ value.

Step 4: Write the reducing agent half-equation in reverse. The two half-equations can now be balanced and then added together to give the overall equation for the spontaneous reaction.

AS 19.1.4
Predict whether a reaction will be spontaneous using standard electrode potential values.
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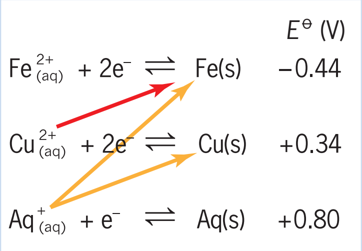

Figure 8.1.9 The arrows indicate the combinations of reactants that will react spontaneously. Of the reactants shown here, Ag^+(aq) will react with Cu(s) and Fe(s), and Cu^{2+}(aq) will only react with Fe(s).

Worked example 2

Predict whether a spontaneous reaction will occur between silver metal and acidified potassium permanganate, $KMnO_4$, solution. If a spontaneous reaction occurs:

a Write half-equations for the oxidation and reduction reactions.

b Write an overall ionic equation.

c Calculate the cell potential.

Solution

a *Step 1:* Write out the equations and $E^\ominus$ values for the reactants listed from the table of standard electrode potentials.

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E^\ominus = +0.80\text{ V}$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\text{ V}$$

Step 2: Highlight the two reactants, noting whether there is an oxidizing agent and a reducing agent present.

$$Ag^+(aq) + e^- \rightleftharpoons \mathbf{Ag(s)} \qquad E^\ominus = +0.80\text{ V}$$
$$\mathbf{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.51\text{ V}$$

Step 3: Referring to the highlighting in the above equations: the oxidizing agent (MnO_4^-) does have a more positive $E^\ominus$ value than the reducing agent, Ag(s), so a spontaneous reaction will occur. Note that MnO_4^- will only react if H^+ ions are present. The description, *acidified* potassium permanganate indicates the presence of $H^+(aq)$.

Step 4: Half-equations for the oxidation and reduction reactions, in order are:

$$\mathbf{Ag(s)} \rightarrow Ag^+(aq) + e^-$$
$$\mathbf{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

b To write a balanced equation for the reaction, the number of electrons must be balanced, so the equation for the oxidation of silver must be multiplied by 5. Note that this does not change the value of the standard electrode potential for Ag/Ag^+.

$$\mathbf{5Ag(s)} \rightarrow 5Ag^+(aq) + 5e^-$$
$$\mathbf{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$

The overall ionic equation for the reaction is:

$$5Ag(s) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Ag^+(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

c The cell potential for the reaction is:

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{oxidizing agent half-cell}} - E^\ominus_{\text{reducing agent half-cell}} \\ &= +1.51 - 0.80 = 0.71\ \text{V} \end{aligned}$$

As mentioned above, it is important to note that the permanganate ion (MnO_4^-) does not act as an oxidizing agent in the above reaction unless the solution is acidified. $H^+(aq)$ ions are an integral part of the reaction process. This is also the case with a number of other species, such as the dichromate ion, $Cr_2O_7^{2-}$, the sulfate ion, SO_4^{2-}, and the nitrate ion, NO_3^-. It is also worth noting that the group 1 cations (Li^+, Na^+ and K^+) do not take part in redox reactions in aqueous solutions because they are weaker oxidizing agents than water. These ions will invariably be spectator ions under these circumstances.

WORKSHEET 8.1
Standard electrode potentials

Worked example 3

Use standard electrode potentials to calculate the cell potential for the following reaction and state whether or not the reaction is spontaneous.

$$2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$$

Solution

Step 1: The half-equations involved here are:

$$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq) \qquad E^\ominus = +0.15\ \text{V}$$
$$Cu^+(aq) + e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.52\ \text{V}$$

Step 2: Highlight the two reactants noting whether there is an oxidizing agent and a reducing agent present.

$$Cu^{2+}(aq) + e^- \rightleftharpoons \mathbf{Cu^+(aq)} \qquad E^\ominus = +0.15\ \text{V}$$
$$\mathbf{Cu^+(aq)} + e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.52\ \text{V}$$

Step 3: Referring to the highlighting in the above equations, the oxidizing agent (Cu^+) has a more positive $E^\ominus$ value than the reducing agent, also Cu^+, so a spontaneous reaction will occur.

The cell potential for the reaction is:

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{oxidizing agent half-cell}} - E^\ominus_{\text{reducing agent half-cell}}$$
$$= +\,0.52 - 0.15 = 0.37\text{ V}$$

Worked example 4

Using calculation of the cell potential, explain why concentrated hydrochloric acid does not react with potassium dichromate(VI).

Solution

The species that may react are $H^+(aq)$ and $Cl^-(aq)$ from the hydrochloric acid and $K^+(aq)$ and $Cr_2O_7^{2-}(aq)$ from the potassium dichromate(VI).

Steps 1 & 2: The half-equations involved are:

$$\mathbf{Cr_2O_7^{2-}(aq)} + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^\ominus = +1.33\text{ V}$$
$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons \mathbf{242Cl^-(aq)} \qquad E^\ominus = +1.36\text{ V}$$

The equation for the reduction of $K^+(aq)$ was not written out because K^+ is a weaker oxidizing agent than water (and much weaker than $Cr_2O_7^{2-}$).

Step 3: Referring to the highlighting in the above equations, the oxidizing agent ($Cr_2O_7^{2-}$) has a *less positive* $E^\ominus$ value than the reducing agent ($Cl^-(aq)$).

The cell potential for the reaction is:

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{oxidizing agent half-cell}} - E^\ominus_{\text{reducing agent half-cell}}$$
$$= +\,1.33 - 1.36 = -0.03\text{ V}$$

This negative cell potential, together with the weakness of Cl^- as a reducing agent means that a spontaneous reaction *will not* occur.

Limitations of the table of standard electrode potentials

While standard electrode potentials are very useful for predicting redox reactions under standard conditions, there are some limitations to this method. Perhaps the most significant of these is that it gives no indication of the *rate* at which a predicted reaction may proceed.

For example, according to the table of standard electrode potentials, hydrogen peroxide (H_2O_2) should react with itself:

$$O_2(g) + 2H^+(aq) + 2e^- \rightarrow \mathbf{H_2O_2}(aq) \qquad E^\circ = +0.68\text{ V}$$
$$\mathbf{H_2O_2}(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l) \qquad E^\circ = +1.78\text{ V}$$
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g) \qquad \text{cell potential} = 1.10\text{ V}$$

Hydrogen peroxide does in fact react with itself, but the rate of reaction at room temperature is very slow. When stored in a brown bottle or in a dark cupboard, the concentration of the hydrogen peroxide is relatively unchanged after several months.

If standard conditions of temperature, pressure and concentration are not being used, the table cannot be relied upon for accuracy, particularly if the electrode potentials are similar (i.e. the species are close to each other in the series). In general, the greater the predicted cell potential, the more likely the predicted reaction is to occur.

Some metals, most notably aluminium, form an impervious oxide layer over the metal that prevents it from reacting. Aluminium is a strong reducing agent and would normally be readily oxidized. Nevertheless, this metal is widely used in the construction industry for, among other uses, the frameworks for aeroplanes and windows. Without its oxide layer to prevent further oxidation, aluminium would not be nearly as useful a structural material as it is.

Section 8.1 Exercises

1 Describe the standard hydrogen electrode, including the conditions under which it operates and draw a diagram of it.

2 Use the standard electrode potentials given for the following oxidizing agent/reducing agent pairs to answer the questions below:

I Sc^{2+}/Sc $E^{\ominus} = -2.12$ V
II Zn^{2+}/Zn $E^{\ominus} = -0.76$ V
III Sn^{4+}/Sn^{2+} $E^{\ominus} = +0.15$ V
IV Ag^{+}/Ag $E^{\ominus} = +0.80$ V
V V^{2+}/V $E^{\ominus} = -1.18$ V
VI Na^{+}/Na $E^{\ominus} = -2.71$ V

a State which species is the:

i strongest oxidizing agent
ii strongest reducing agent

b Rewrite the list of half-cells in order of decreasing reducing agent strength, i.e. from strongest to weakest reducing agent.

3 From figure 8.1.7, identify a substance that will oxidize iodide ions, but not bromide ions. Explain your choice and write an equation for the redox reaction that will occur.

4 Draw and label a diagram showing the arrangement of equipment which could be used to measure the standard electrode potential of tin, Sn.

5 A voltaic cell was set up using aluminium in aluminium sulfate solution and copper in copper sulfate solution, with both solutions being under standard conditions.

a Calculate the cell potential.

b Write an ionic equation for the spontaneous cell reaction.

6 A voltaic cell is constructed using half-cells of Cu^{2+}/Cu and Ni^{2+}/Ni.

a Draw a diagram of this voltaic cell and clearly label the:

i anode and cathode
ii polarity of the electrodes
iii oxidizing agent and reducing agent
iv direction of flow of electrons through the connecting wires.

- **b** **i** Write the oxidation and reduction half-equations for the voltaic cell described in part **a**.
  - **ii** Write the overall ionic equation for that cell.
  - **iii** Calculate its cell potential.

7 **a** Give two reasons why a half-cell may require the use of an inert electrode such as graphite or platinum.

b Write half-equations for three half-cells that use an inert electrode.

c What is the main advantage of using graphite rather than platinum as an electrode material?

8 For each of the following situations, use figure 8.1.7 to determine whether or not a spontaneous reaction will occur by calculating the cell potential. If a spontaneous reaction does occur, write an overall ionic equation for the process.

a Zinc chloride solution is stored in an iron container.

b Magnesium ribbon is added to a zinc iodide solution.

c Bromine liquid is poured into magnesium chloride solution.

d Sodium metal is dropped into a beaker of water.

9 Strips of lead are placed into separate beakers containing solutions of $CuSO_4$, $SnCl_2$, $Fe(NO_3)_2$, $AgNO_3$ and $PbCl_2$. In which beaker(s) will a metal coating form on the lead strips?

10 A strip of aluminium foil is placed into a beaker containing a solution of nickel nitrate. According to figure 8.1.7, a reaction should occur; however, no reaction is observed. Explain this observation.

8.2 ELECTROLYSIS

The majority of reactions in *voltaic cells* occur in an aqueous environment, although water is not directly involved as a reactant. Water can undergo both oxidation and reduction—it is a weak oxidizing agent and weak reducing agent—it only undergoes redox reactions with highly reactive substances, such as chlorine, sodium and potassium. The reactions occurring in *electrolytic cells* often involve weak oxidizing agents and reducing agents that are forced to undergo reaction by the supply of electrical energy. When a pure molten substance such as sodium chloride is electrolysed, the products are somewhat obvious. The electrolyte is made up of two ions only, so there is only one possible oxidizing agent, $Na^+(l)$, and one possible reducing agent, $Cl^-(l)$. The weakness of Na^+ as an oxidizing agent or Cl^- as a reducing agent does not matter.

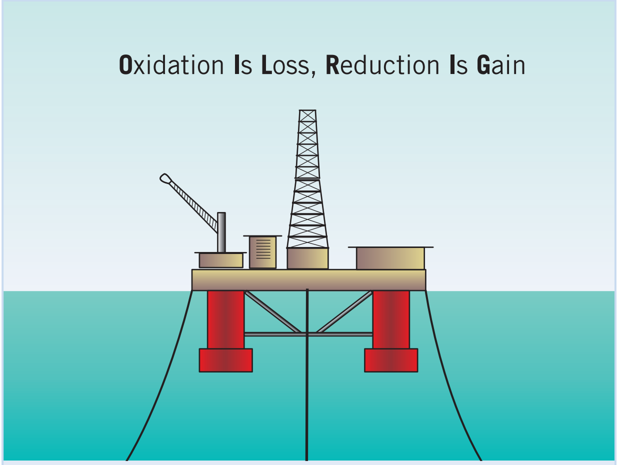

Figure 8.2.1 Recall that oxidation is loss of electrons and reduction is gain of electrons.

In electrolysis, one electrode is connected to the positive terminal of the power supply and the other is connected to the negative terminal. Hence one electrode, the negative electrode, is a supplier of electrons (**electron source**) and will attract positively charged ions in the electrolyte, while the positive electrode, is an **electron sink** (will take electrons) and will attract negatively charged ions in the electrolyte.

Since oxidation is the loss of electrons, it occurs at the positive electrode in electrolysis (the anode). Only reducing agents can be oxidized, so only negatively charged reducing agents (and water) can react at the positive electrode. Similarly, reduction is the gain of electrons and this occurs at the negative electrode in electrolysis (the cathode). Only oxidizing agents can be reduced, so only positively charged oxidizing agents (and water) can react at the negative electrode.

Don't let this be confusing to you! Table 8.2.1 summarizes these requirements.

Interactive Animation
Electrolysis

TABLE 8.2.1 SUMMARY OF ELECTROLYSIS

Negative electrode (electron source)	Positive electrode (electron sink)
• Attracts positive ions • Electrons are gained • This is called reduction • And usually occurs to an oxidizing agent • Reaction occurs if positive ion is an oxidizing agent (found on left-hand side of table of standard electrode potentials)	• Attracts negative ions • Electrons are lost • This is called oxidation • And usually occurs to a reducing agent • Reaction occurs if negative ion is a reducing agent (found on right-hand side of table of standard electrode potentials)

CHEM COMPLEMENT

Isolating fluorine

As one of the most reactive elements in the periodic table, fluorine was an extremely difficult element to isolate from its compounds. Many chemists were poisoned (including Humphry Davy) and some even died in their attempts! French chemist Henri Moissan (1852–1907) was the intrepid chemist who finally triumphed by electrolysing a solution of potassium hydrogen fluoride KHF_2 dissolved in a pure liquid called anhydrous hydrogen fluoride (AHF). The fluorine was produced at the anode and hydrogen was made at the cathode. The extremely explosive reaction between these two gases made it essential to keep them separate. The electrolysis cell was a U-shaped tube with an electrode in each side of the U. The tube was kept at a temperature below –23°C and the fluorine and hydrogen were passed through to be stored in two different tubes.

Initially the only material would hold the extremely corrosive AHF solution was made of an alloy of platinum and iridium; however, Moissan later found that copper vessels could also be used, since the inside of the vessel became coated with a protective layer of copper(II) fluoride.

In modern times the extreme reactivity of fluorine and hydrogen fluoride has remained problematic, with reaction vessels needing to be made of stainless steel (in which it is difficult to see what you are doing), a non-reactive polymer called kel-F (somewhat translucent) and synthetic sapphire (quite transparent, but extremely expensive and brittle).

Figure 8.2.2 Henri Moissan isolated fluorine in 1886.

Electrolysis of aqueous solutions

Whenever an aqueous solution of a compound is electrolysed, it is possible that water will be involved in the reaction at either or both electrodes. Water is a polar molecule, so will be attracted to either the positive electrode or the negative electrode. For this reason, when predicting the products of reaction in an electrolytic cell involving an aqueous solution, we must consider the oxidation and reduction reactions for water:

19.2.1 Predict and explain the products of electrolysis of aqueous solutions. © IBO 2007

$$H_2O(l) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) + OH^-(aq) \qquad E^\ominus = -0.83\text{ V}$$

$$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l) \qquad E^\ominus = +1.23\text{ V}$$

The following steps should be followed when determining which reactions occur during an electrolysis process:

Electroylisis of water

Step 1: Draw up two columns on your page. Give one column the heading 'Positive electrode' and the other 'Negative electrode'. Under each heading make a list of ions in the electrolyte that will be attracted to that electrode, remembering to always include water in the list.

Step 2: Locate and highlight each of the species that you have listed on the table of standard electrode potentials (figure 8.1.7, p. 249).

Step 3: Remembering that only negatively charged reducing agents (and water) can react at the positive electrode, find the best reducing agent (most negative $E^\ominus$ value) on your list for the positive electrode and write out the half-equation for its oxidation.

Step 4: Remembering that only positively charged oxidizing agents (and water) can react at the negative electrode, find the best oxidizing agent (most positive $E^\ominus$ value) on your list for the negative electrode and write out the half-equation for its reduction.

Worked example 1

Determine the products formed at each inert electrode during the electrolysis of a 1 mol dm^{-3} magnesium iodide solution. Draw a diagram of the electrolytic cell used and annotate the diagram to show the:

- polarity of the electrodes
- anode and cathode
- oxidizing agent and reducing agent
- oxidation and reduction reactions
- overall equation representing the cell reaction.

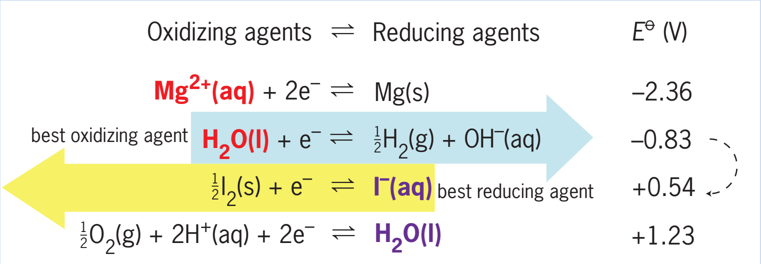

Figure 8.2.3 The electrochemical series can be used to determine the reactions that occur in an electrolytic cell containing $MgI_2(aq)$.

Solution

Step 1:

Positive electrode	Negative electrode
$I^-(aq)$	$Mg^{2+}(aq)$
$H_2O(l)$	$H_2O(l)$

Step 2:

	$E^\ominus$ (V)
$\mathbf{Mg^{2+}(aq)} + 2e^- \rightleftharpoons Mg(s)$	–2.36
$\mathbf{H_2O(l)} + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$\tfrac{1}{2}I_2(s) + e^- \rightleftharpoons \mathbf{I^-(aq)}$	+0.54
$\tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons \mathbf{H_2O(l)}$	+1.23

Step 3: $I^-(aq)$ is the best reducing agent (with the most negative, or lowest, $E^{\ominus}$ value) reacting at the positive electrode. The equation for the reaction occurring at the positive electrode (oxidation of I^-) is:

$$I^-(aq) \rightarrow \tfrac{1}{2} I_2(s) + e^-$$

Step 4: $H_2O(l)$ is the best oxidizing agent (with the most positive, or highest, $E^{\ominus}$ value) reacting at the negative electrode. The equation for the reaction occurring at the negative electrode (reduction of H_2O) is:

$$H_2O(l) + e^- \rightleftharpoons \tfrac{1}{2} H_2(g) + OH^-(aq)$$

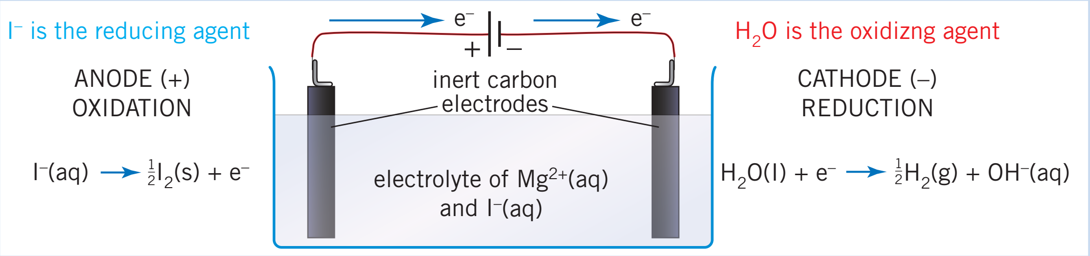

Figure 8.2.4 The electrolysis of $MgI_2(aq)$.

For the overall reaction to occur, the cell would require a minimum of 1.37 V ($E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}} = 0.54 + 0.83$ V) to be supplied (under standard conditions):

$$H_2O(l) + I^-(aq) \rightarrow \tfrac{1}{2} I_2(aq) + \tfrac{1}{2} H_2(g) + OH^-(aq)$$

Worked example 2

Determine the products formed at each inert electrode during the electrolysis of an aqueous mixture of 1 mol dm^{-3} copper(II) sulfate and 1 mol dm^{-3} zinc bromide, given that the electrolysis was allowed to proceed for a considerable length of time.

a Draw a diagram of the electrolytic cell used, and show on or below the diagram the:

- polarity of the electrodes
- anode and the cathode
- oxidation and reduction reactions
- oxidizing agent and the reducing agent
- overall equation representing the cell reaction.

b State any changes to reaction products that may occur after a prolonged period of operation of the cell.

Solution

Step 1:

Positive electrode	Negative electrode
$SO_4^{2-}(aq)$	$Cu^{2+}(aq)$
$Br^-(aq)$	$Zn^{2+}(aq)$
$H_2O(l)$	$H_2O(l)$

Step 2: Note that SO_4^{2-} is unable to react at the positive electrode, as it is an oxidizing agent (and $H^+(aq)$ is absent):

$$\mathbf{SO_4^{2-}(aq)} + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$$

	E° (V)
$\mathbf{H_2O(l)} + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$\mathbf{Zn^{2+}(aq)} + 2e^- \rightleftharpoons Zn(s)$	–0.76
$\mathbf{Cu^{2+}(aq)} + 2e^- \rightleftharpoons Cu(s)$	+0.34
$\frac{1}{2}Br_2(l) + e^- \rightleftharpoons \mathbf{Br^-(aq)}$	+1.09
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons \mathbf{H_2O(l)}$	+1.23

Step 3: $Br^-(aq)$ is the best reducing agent (with the most negative, or lowest, $E^\ominus$ value) reacting at the positive electrode. The equation for the reaction occurring at the positive electrode (oxidation of Br^-) is:

$$Br^-(aq) \rightarrow \frac{1}{2}Br_2(l) + e^-$$

Step 4: $Cu^{2+}(aq)$ is the best oxidizing agent (with the most positive, or highest, $E^\ominus$ value) reacting at the negative electrode. The equation for the reaction occurring at the negative electrode (reduction of Cu^{2+}) is:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

a The annotated diagram is shown below.

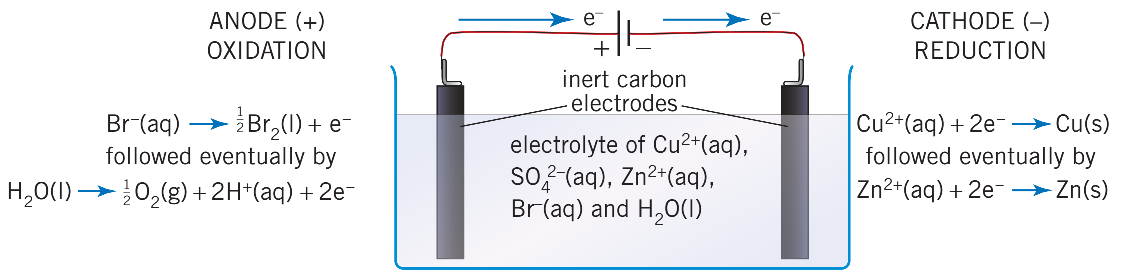

Figure 8.2.5 The electrolysis of $CuSO_4(aq)$ and $ZnBr_2(aq)$.

For the overall reaction to occur, the cell would require a minimum of 0.75 V ($E^\ominus_{cell} = E^\ominus_{\text{oxidizing agent half-cell}} - E^\ominus_{\text{reducing agent half-cell}} = 1.09 - 0.34$ V) to be supplied (under standard conditions):

$$Cu^{2+}(aq) + 2Br^-(aq) \rightarrow Cu(s) + Br_2(l)$$

b If the reaction was allowed to proceed for some time, eventually the concentrations of Cu^{2+} and Br^- would decrease sufficiently that the next strongest oxidizing agent and reducing agent would undergo reaction. In this case, zinc ions would undergo reduction at the cathode to form zinc metal, and water would be oxidized at the anode to produce oxygen gas and hydrogen ions. The sequence of reactions is:

At the cathode (–), reduction occurs:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

followed eventually by:

$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$$

Then, if all of the $Zn^{2+}(aq)$ ions were consumed, finally water would undergo reduction:

$$H_2O(l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-(aq)$$

At the anode, oxidation occurs:

$$Br^-(aq) \rightarrow \tfrac{1}{2}Br_2(l) + e^-$$

Followed eventually by:

$$H_2O(l) \rightarrow \tfrac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

De

DEMO 8.1
Electrolysis with a voltameter

In a practical context, aqueous electrolysis is the primary method for the production of oxygen and hydrogen. In the laboratory, a voltameter is used to electrolyse a dilute solution such as $NaNO_3$, producing hydrogen and oxygen in the ratio 2 : 1.

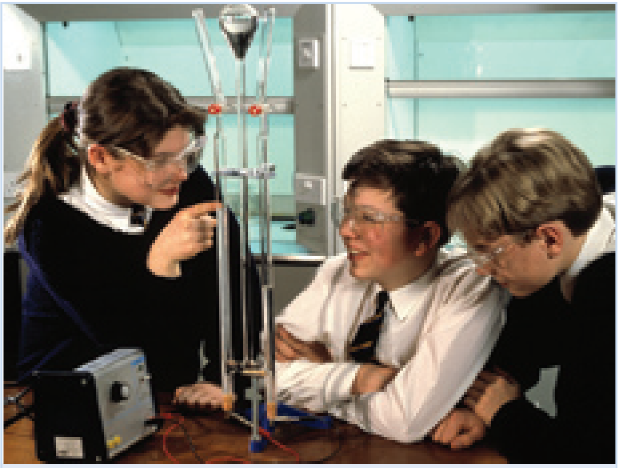

Figure 8.2.6 A voltameter is used to electrolyse aqueous solutions and to collect the gases produced.

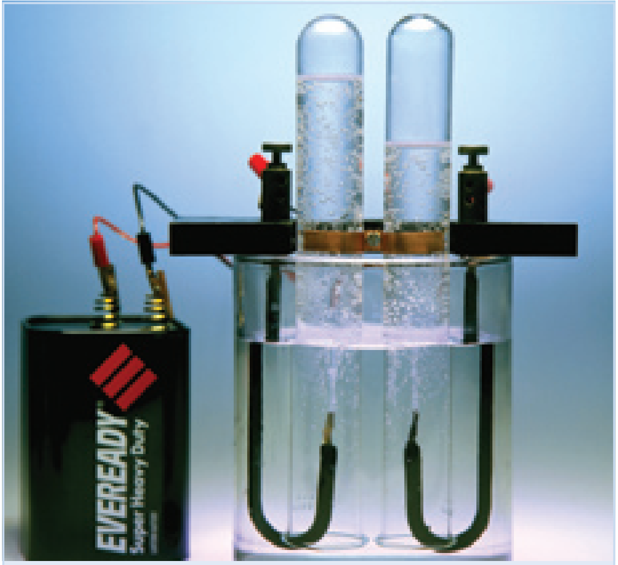

Figure 8.2.7 The electrolysis of a dilute solution such as $NaNO_3$ produces oxygen and hydrogen in the molar (and volume) ratio of 1 : 2.

The products of aqueous electrolysis may be identified by a number of tests. The evolution of a gaseous product is easily identified by bubbles appearing at the electrode. The identity of the gas needs to be decided by further testing. When water is reduced (at the cathode, the negative electrode) according to the equation:

$$H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$$

Hydrogen gas is evolved and the addition of hydroxide ions to the solution increases the pH of the solution surrounding the electrode. When universal indicator is added to the solution, a purple colour is observed in the solution surrounding the negative electrode.

When water is oxidized (at the anode, the positive electrode) according to the equation

$$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

oxygen gas is evolved and the production of $H^+(aq)$ decreases the pH of the solution surrounding the electrode. When universal indicator is added to the solution, a red colour is observed in the solution surrounding the positive electrode.

The evolution of chlorine gas is easily detected by smell, although this must be done with extreme caution. Preferably, the presence of chlorine can be confirmed by testing with damp litmus paper, which chlorine will bleach.

When a metal such as copper is the product of aqueous electrolysis, it usually coats the negative electrode, and the production of iodine at the positive electrode can easily be seen by the distinctive brown colour appearing at and falling away from the electrode. (See photo on chapter introduction page.)

One other factor must be considered as an influence on the products of aqueous electrolysis. This factor is the nature of the electrode. Usually the electrodes used in aqueous electrolysis are inert graphite or platinum electrodes; however, this does not have to be the case. Metal electrodes may be used for electrolysis. If this is the case, the metal of the electrode needs to be considered at the positive electrode as a possible reducing agent.

Figure 8.2.8 When water is reduced, hydroxide ions increase the pH of the solution (on right) and when it is oxidized, hydrogen ions decrease the pH of the solution (on left).

PRAC 8.1
Electrolysis of aqueous solutions

Worked example 3

An aqueous solution of nickel sulfate was electrolysed using copper electrodes. Deduce the products at the positive and negative electrodes and hence write the equations for oxidation and reduction occurring in the electrolysis cell.

Solution

Step 1:	Positive electrode	Negative electrode
	$Cu(s)$	$Ni^{2+}(aq)$
	SO_4^{2-}	
	$H_2O(l)$	$H_2O(l)$

Step 2: Note that SO_4^{2-} is unable to react at the positive electrode, as it is an oxidizing agent (and $H^+(aq)$ is absent).

	$E^\ominus$ (V)
$\mathbf{H_2O(l)} + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$\mathbf{Ni^{2+}(aq)} + 2e^- \rightleftharpoons Ni(s)$	–0.23
$Cu^{2+}(aq) + 2e^- \rightleftharpoons \mathbf{Cu(s)}$	+0.34
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons \mathbf{H_2O(l)}$	+1.23

Step 3: Cu(s) is the best reducing agent (with the most negative, or lowest, $E^\ominus$ value) reacting at the positive electrode. The equation for the reaction occurring at the positive electrode (oxidation of Cu) is:

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

This means that the actual copper electrode will be used up as the electrolysis proceeds.

Step 4: $Ni^{2+}(aq)$ is the best oxidizing agent (with the most positive, or highest, $E^\ominus$ value) reacting at the negative electrode. The equation for the reaction occurring at the negative electrode (reduction of Ni^{2+}) is:

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

A coating of nickel will appear on the negative electrode as the electrolysis proceeds.

THEORY OF KNOWLEDGE

Being able to make detailed qualitative and quantitative observations using our five senses is an important part of evidence collection in science. Consider an experiment involving a chemical reaction you have carried out in this topic for which sense perception was important.

- Sense perception is selective; some things we notice, others we overlook altogether. With so many different kinds of observations possible in a chemical reaction, how do you distinguish between those that are chemically significant and those that are not?
- Do you find that the observations you make may differ from those of other students in the class?
- Do you think the combined observations of many students are better than those of an individual?
- How has your ability to use your senses to collect evidence changed over the course of your IB Chemistry studies? Have you become a more expert observer?
- Can you give an example where your expectations, what you were expecting to happen, influenced the sorts of observations you made?
- How do scientists ensure that they don't make hasty conclusions based on insufficient evidence?
- Technology gives us access to devices that allow us to make observations beyond the range with normal sense of sight can provide. Can you give some examples of such devices that you have used?
- We rely so much on our senses that it is reflected in figures of speech we use. For example we use 'insight', 'seeing is believing', 'nonsense' and 'I'll believe it when I see it'. Can you think of any other figures of speech that connect what we know to our senses?

Electrolysis under non-standard conditions

In the examples considered so far, the solutions being electrolysed have been at standard conditions: 25°C, 1.01×10^2 kPa pressure and 1 mol dm^{-3} concentration. Can we predict what reactions would occur at the electrodes of an electrochemical cell if conditions are not standard? It should be recognized that the electrode potentials provided in the table of standard electrode potentials will not be reliable under non-standard conditions, particularly if the $E^\ominus$ values for possible reactions are similar. An important application of this phenomenon involves the electrolysis of solutions of sodium chloride of different concentrations. Highly concentrated solutions of sodium chloride are also known as brine. The industrial preparation of sodium hydroxide and chlorine gas utilizes the electrolysis of concentrated brine, and this process serves as an example of the concentration dependence of electrolysis.

When an aqueous solution of sodium chloride is electrolysed under standard conditions, with [NaCl] = 1.0 mol dm^{-3}, gases are evolved at each electrode. When the possible oxidizing agents are considered, water is a better oxidizing agent than $Na^+(aq)$:

$$H_2O(l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-(aq)$$

so the gaseous product at the negative electrode is hydrogen gas.

Indeed, no matter what the concentration of a sodium chloride solution, the reduction reaction is always that given above.

When trying to identify the oxidation reaction we need to consider the following two equations:

$$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \qquad E^\ominus = +1.33\ V$$

$$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^- \qquad E^\ominus = +1.36\ V$$

The standard electrode potential of the two reactions is very close indeed. Experimentally, both chlorine and oxygen may be detected as products.

A very dilute solution of sodium chloride will only produce oxygen and hydrogen ions at the anode; no chlorine is detected at all, while a concentrated solution of sodium chloride (i.e. significantly greater than 1.0 mol dm^{-3}) produces only chlorine as the product of oxidation. At concentrations between these points, a mixture of both chlorine gas and oxygen gas is produced at the anode. In comparison, you will recall that molten sodium chloride produces sodium metal at the cathode and chlorine gas at the anode.

Factors affecting the relative amounts of products formed during electrolysis

CHEM COMPLEMENT

Michael Faraday

Michael Faraday (1791–1867) was born to a poor family and received no significant education. At the age of 13, he obtained a job helping in a bookshop. This access to books enabled him to educate himself. He was 22 years old when an explosion in Humphry Davy's laboratory injured an assistant and led to Faraday being able to fill the position. He was fascinated with electricity, so it was almost inevitable that he would extend the work of Davy to calculate the masses of material formed in electrolytic cells. In addition to his work on electricity, Faraday was the first to investigate electromagnetic induction and build a dynamo—the precursor to the modern power generator. He also made the first gas-fired heating device that came to be known as the Bunsen burner.

Figure 8.2.9 Michael Faraday (1791–1867).

In the electrolysis of molten NaCl, the reaction at the cathode is:

$$Na^+(l) + e^- \rightarrow Na(l)$$

For every mole of sodium atoms that are formed, one mole of electrons must be supplied by the power source.

When molten copper(II) chloride is electrolysed, the reaction at the cathode is:

$$Cu^{2+}(l) + 2e^- \rightarrow Cu(l)$$

Because the charge on the copper ion is 2+, two mole of electrons are required for every one mole of copper atoms formed.

Predictably, when molten chromium(III) sulfate is electrolysed, the reaction at the cathode is

$$Cr^{3+}(l) + 3e^- \rightarrow Cr(l)$$

Three mole of electrons are required per mole of chromium atoms produced.

The greater the charge on the cation, the greater the amount of electrons required to deposit one mole of metal at the cathode.

WORKSHEET 8.2
Electrolysis reactions

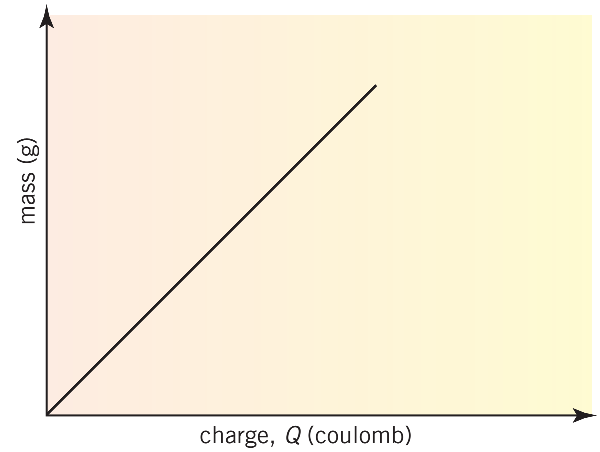

Figure 8.2.10 The relationship between the mass of product and quantity of charge.

119.2.2
Determine the relative amounts of the products formed during electrolysis.
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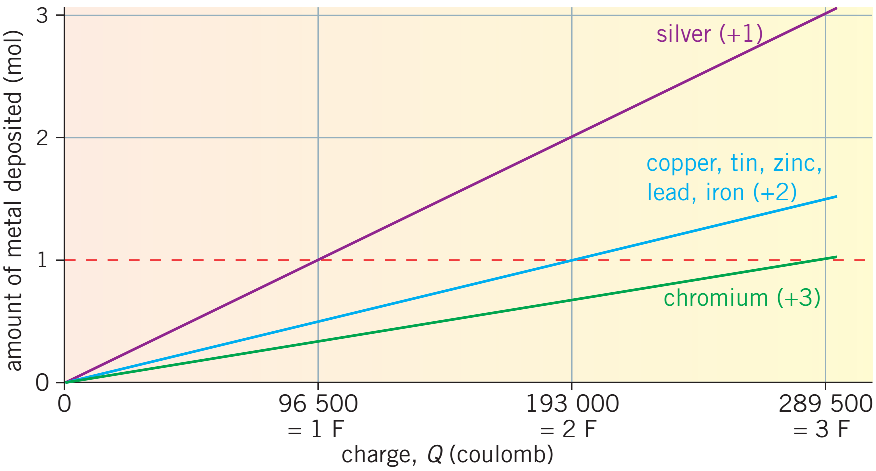


Figure 8.2.11 Faraday's first law of electrolysis, $m \propto Q$.

In the case of non-metals such as chlorine and oxygen, the amount of electrons required to produce one mole of the element again depends on the charge on the ion, although it may also depend on the number of atoms in one molecule of the element:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

$$2O^{2-}(aq) \rightarrow O_2(g) + 4e^-$$

Assuming that the charge on the ions remains constant, if the amount of electrons passing through the electrolysis circuit increases, we can expect the amount of product made and hence the mass produced at the electrode to also increase.

Electrons are the fundamental units of electric charge and each electron carries a charge of 1.6021×10^{-19} coulomb (C). But how are we to measure the amount of charge that flows through a cell? This can be done by measuring the current flow (measured in ampere, or C s^{-1}) and the time during which the current flows (measured in s).

PRAC 8.2
Factors affecting the amount of product made in electrolysis

Mathematically: $Q = I \times t$

where I = current in amperes (C s^{-1})
Q = amount of electric charge (C)
t = time (s)

So we can see that the amount of product made at an electrode depends upon the amount of charge flowing through the electrolysis circuit, which is dependent on the current flowing through the circuit and the time for which the current is flowing (the duration of the electrolysis experiment).

TABLE 8.2.2 SUMMARY OF FACTORS AFFECTING RELATIVE AMOUNT OF PRODUCTS FORMED DURING ELECTROLYSIS

Factor	Increases	Decreases
Charge on ion	Amount of product decreases	Amount of product increases
Current flowing through circuit	Amount of product increases	Amount of product decreases
Duration of electrolysis	Amount of product increases	Amount of product decreases

CHEM COMPLEMENT

Calculating the actual amount produced during electrolysis

The amount of charge carried by one mole of electrons is defined as one faraday (symbol F), which is approximately 96 500 C.

Mathematically: $n(\text{e}) = \dfrac{Q}{F}$

where F = Faraday's constant (C mol^{-1})
Q = amount of electric charge (C)
$n(\text{e})$ = amount of electrons (mol)

Faraday's first law of electrolysis states:

> The mass of metal deposited at the cathode is directly proportional to the quantity of electricity passed through the cell.

Mathematically: $m \propto Q$

where Q = amount of electric charge (C)
m = mass of metal (g)

Faraday's second law of electrolysis states:

> In order to produce one mole of product in an electrolysis cell, a whole number of mole of electrons must be supplied.

Faraday's laws together give us the relationship

$$n(\text{element}) = \frac{1}{x} \times \frac{Q}{F}$$

where x = amount (in mol) of electrons required to produce one mol of the element
Q = amount of electric charge (C)
F = Faraday's constant

Electroplating

AS 19.2.3 Describe the use of electrolysis in electroplating. © IBO 2007

In 1805, just five years after Volta invented the first battery, Luigi Brugnatelli (1761–1818) developed a technique for plating a thin layer of gold over large silver objects. The era of electroplating more expensive or durable metals over a base metal had arrived! By the 1850s, the technique was reasonably refined, and the **electrodeposition** of silver onto teapots, serving platters and cutlery was common, particularly in England. Modern techniques allow for the deposition of a layer of metal such as platinum, ruthenium or osmium onto electronic circuitry components as thin as one-millionth of a centimetre. Cyanide-based electrolytes are still widely used, and need to be handled carefully because of their toxicity.

Figure 8.2.12 Spoons to be electroplated are prepared for an electrolyte bath.

Electroplating offers the opportunity of coating a metal object with a thin layer of another metal that has particular properties such as attractiveness, durability or enhanced electrical and heat conduction. The cost of the energy required to plate the metal object is offset by the savings in the cost of manufacturing the entire object of the more desirable metal. Careful control of the current flow through the cell and selection of an appropriate electrolyte ensures that an even layer of the coating metal is deposited. Applications of electroplating include:

- Jewellery—A gold bracelet may not be made entirely from gold, as pure gold is soft and expensive. A cheaper, harder metal is often used to form the object and the object is then plated with gold. In this case, the main purpose of electroplating is to enhance the appearance of the object.
- Tin cans for food—Food cans are usually made from steel coated with tin. The steel is relatively cheap and it is strong enough to retain its shape during handling. The acidity of many fruits would cause the contents to react with the steel, so a layer of less reactive tin is plated onto the steel to prevent this from happening. In this case, the main purpose of electroplating is to protect the underlying metal.
- Car parts and tools—The plating of nickel and chromium is a common practice in many industries, as these metals protect base metals (such as steel) from corrosion and ensure smooth, low-friction surfaces for such items as engine bearings. The owners of many high-performance vehicles make extensive use of chromium to highlight components of their cars, such as bumper bars and rocker covers.
- Galvanizing (zinc coating)—Zinc forms a very effective coating on iron as it limits corrosion. This is referred to as galvanizing. Industry uses large quantities of galvanized iron, wire and piping. Car bodies are also coated with zinc before they are painted, in order to inhibit corrosion.

DEMO 8.2 Electroplating

In all electroplating applications, the item to be plated is connected to the negative electrode so that the metal cations in the electrolyte will undergo reduction. A large block of the metal used as the coating constitutes the anode, and the electrolyte solution may be a salt of this metal or, more commonly in industrial practice, a cyanide solution. Unlike examples of other cells considered so far in which inert graphite or platinum are used, in electroplating cells it is common to use electrodes that actively take part in the reactions.

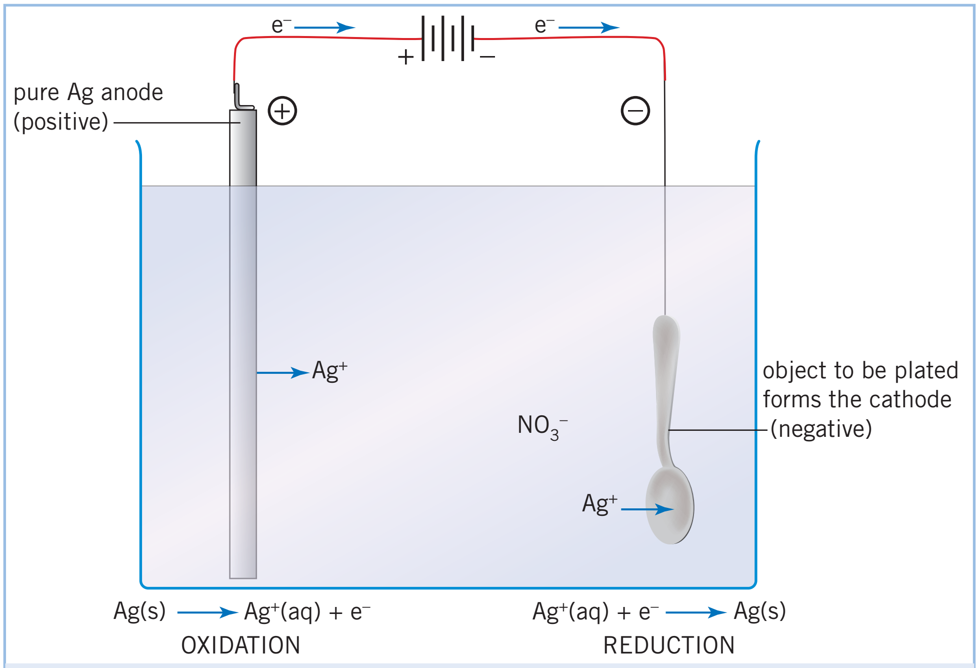


Figure 8.2.14 An electrolytic cell for electroplating a spoon.

As the metal anode dissolves, it releases cations into solution, which then migrate to the cathode and are reduced back to the metal. In this way, the concentration of ions in the electrolyte remains fairly constant and the reactions can proceed without interruption until the anode has been consumed. In practice, the exact composition and concentration of the electrolyte, current density, temperature and so on must be carefully controlled to ensure a uniform coating of the metal being plated.

CHEM COMPLEMENT

The humble tin can

The invention of the 'tin can', a sealed steel container that can be electroplated with tin to protect the steel from reaction with food acids, revolutionized the preservation of foods across the world. A thin coating of tin is used to protect the steel from reacting with the air or other substances with which it is in contact. Englishman Peter Durand invented the first tin-plated steel cans in 1810, although these were handmade and therefore very expensive. It was not until the late 19th century that tin cans were manufactured by machine. A layer of tin of thickness 0.03–0.05 mm is plated onto the steel used in food preservation to make tin cans, as well as automotive bearings and electronic circuits. In all of these applications, tin is used because it is non-toxic and reacts only slowly with air and other substances. Tin provides only passive protection; it is a weaker reducing agent than iron and so cannot protect the base metal once the surface has been broken.

Figure 8.2.13 A tin can — better described as an electroplated steel can

Worked example 4

Explain why electrolysis of aqueous aluminium nitrate is not used for coating objects with aluminium, while aqueous silver nitrate can be used for coating objects with silver.

Solution

Consider the standard electrode potentials for the three species that are present at the cathode in these two cases.

	$E^\ominus$ (V)
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al$	−1.66
$H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	−0.83
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

When an aqueous solution of aluminium nitrate is electrolysed, the best oxidizing agent present is water, with a standard electrode potential of −0.83 V. Therefore aluminium cannot be coated onto the negative electrode from an aqueous solution. However, when an aqueous solution of silver nitrate is electrolysed, $Ag^+(aq)$ is a better oxidizing agent than water, so silver coats onto the cathode.

In worked example 4, it was noted that aluminium cannot be electroplated from an aqueous solution of an aluminium salt. Indeed this is the case for any metal with a standard electrode potential below that of water. Whenever ions such as Mg^{2+}, Na^+, Ca^{2+}, K^+ or Li^+ are in aqueous solution, reduction of water occurs at the cathode, rather than of the metal ion.

Section 8.2 Exercises

1 State, with the correct standard electrode potential, the half-equation for the:

  a oxidation of water

  b reduction of water.

2 Using the standard electrode potentials in figure 8.1.7, identify which of the following elements could be produced by the electrolysis of an aqueous solution of the salt named.

  I Nickel metal from nickel chloride
  II Magnesium metal from magnesium nitrate
  III Silver metal from silver nitrate
  IV Fluorine gas from lithium fluoride
  V Iodine from sodium iodide

3 **a** Determine the products formed at each inert graphite electrode during the electrolysis of an aqueous solution of 1 mol dm^{-3} tin(II) bromide.

  b Draw a diagram of the electrolytic cell used and annotate the diagram with the:

    i polarity of the electrodes
    ii anode and the cathode
    iii oxidation and reduction reactions

  - **iv** oxidizing agent and the reducing agent
  - **v** overall equation representing the cell reaction.

- **c** describe the observations that you would make during this electrolysis.

4 **a** Determine the products that would be formed at each graphite electrode during the electrolysis of an aqueous solution of 1 mol dm^{-3} potassium fluoride.

b Describe the observations that you would make during this electrolysis experiment.

5 Classify each of the following statements as true or false.

a Voltaic cells convert chemical potential energy into electrical energy, while electrolytic cells convert electrical energy into chemical potential energy.

b The anode is always positively charged in voltaic and in electrolytic cells.

c The electrolysis of aqueous 1 mol dm^{-3} iron(II) chloride will result in only oxygen gas being formed at the anode.

d The electrolysis of aqueous aluminium fluoride results in the reduction of Al^{3+} cations to aluminium metal at the cathode.

e The electrolysis of an aqueous solution of NaCl always results in the formation of oxygen gas at the anode.

6 Link the 'Occurrence' statement with the appropriate 'Situation' statement below. Each 'situation' statement may only be used once.

Occurrence	Situation
Potassium metal forms at the cathode	Electrolysis of highly concentrated aqueous potassium chloride solution
Reduction occurs at the cathode	Electrolysis of aqueous lead(II) nitrate solution
Hydrogen gas forms at the cathode	Electrolysis of molten potassium bromide
pH decreases at one electrode	Electrolysis of aqueous 1 mol dm^{-3} lithium iodide solution
Chlorine gas forms at the anode	Any voltaic cell or electrolytic cell

7 Predict the products that would form at the anode and the cathode during electrolysis of the following aqueous solutions.

a 1 mol dm^{-3} copper iodide

b 1 mol dm^{-3} nitric acid

c 2 mol dm^{-3} magnesium chloride

d 1 mol dm^{-3} zinc fluoride

8 An aqueous solution of iron(II) chloride is electrolysed for 10 minutes with a current of 10 amps.

In each of the following cases, describe how the change will affect the amount of product made at the cathode.

a The time taken for electrolysis is increased to 20 minutes.

b The current used in the electrolysis is decreased to 6 amps.

c A solution of iron(III) chloride is used instead of iron(II) chloride.

9 Place the following solutions (I, II, III and IV) in order from smallest to largest in terms of the amount (in mol) of metal that will be produced at the cathode when they are electrolysed for the same period of time and with the same current flowing through the electrolysis cell.

I 0.1 mol dm^{-3} solution of copper(II) sulfate
II 0.2 mol dm^{-3} solution of potassium chloride
III 0.1 mol dm^{-3} solution of chromium(III) nitrate
IV 0.1 mol dm^{-3} solution of silver nitrate

10 A student wishes to plate silver metal onto a steel medallion. A 12 V power supply, a beaker containing 1 mol dm^{-3} silver nitrate ($AgNO_3$), silver electrodes and suitable connecting wires are provided.

a Draw a diagram of the cell that would need to be constructed to achieve this aim.

b Indicate on the diagram the polarity of the electrode (positive or negative) to which the medallion should be attached.

c Indicate which electrode is the cathode and which is the anode.

d Write half-equations to represent the reactions occurring at each electrode.

Chapter 8 Summary

Terms and definitions

Cell potential This is equal to the difference between the electrode potentials of the two half-cells of which the cell is composed.

Electrodeposition The coating of a solid product onto an electrode during electrolysis.

Electrolyte A liquid that can conduct an electric current.

Electromotive force (emf) The amount of energy delivered to electrons in a voltaic cell under standard conditions.

Electron sink Positive terminal of a power source.

Electron source Negative terminal of a power source.

Potential difference Voltage difference between two points which will cause current to flow in a closed circuit.

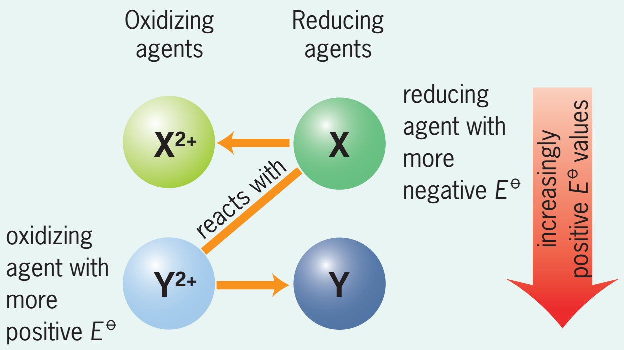
Standard conditions Solutions having a concentration of 1.0 mol dm^{-3}, gases at a pressure of 1.01×10^2 kPa and temperature of 298 K.

Standard electrode potential ($E^{\ominus}$) The potential difference generated by a voltaic cell when a particular half-cell is connected to a standard hydrogen electrode.

Standard hydrogen electrode (standard hydrogen half-cell) A half-cell composed of $H^+(aq)/H_2(g)$ under standard conditions.

Concepts

- The standard hydrogen electrode is made up of a platinum electrode, covered in platinum black, dipping into a 1.0 mol dm^{-3} solution of $H^+(aq)$, with hydrogen gas delivered past the electrode to the solution at a pressure of 1.01×10^2 kPa at 298 K.
- The relative reactivities of chemical species is summarized in the table of standard electrode potentials.
- The standard hydrogen electrode is assigned an electrode potential value of 0.00 V.
- The standard electrode potential for an element is determined by comparing the half-cell containing that element and its conjugate redox pair with the standard hydrogen electrode.
- The table of standard electrode potentials can be used to predict whether a spontaneous reaction will occur between a particular combination of chemicals.

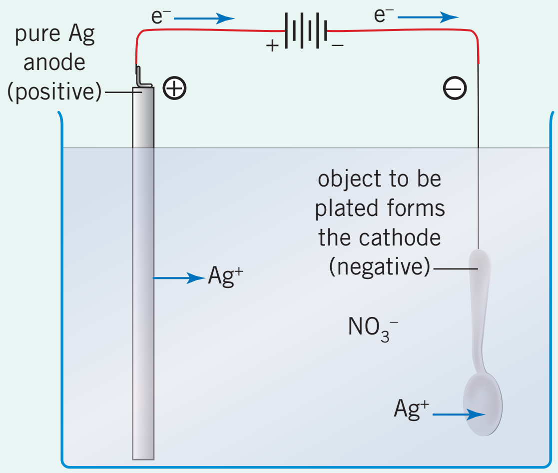


- The cell potential under standard conditions can be determined by the rule:

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{oxidizing agent half-cell}} - E^{\ominus}_{\text{reducing agent half-cell}}$$

- The calculation of cell potential is only a predictor. An expected reaction may not occur, due to other factors such as a slow rate of reaction or non-standard conditions being used.
- Electrolysis is the process of using an external power supply to cause endothermic redox reactions to occur. Electrical energy is converted to chemical potential energy.
- The products of an electrolysis reaction can be predicted from the electrochemical series. In general, the strongest oxidizing agent is reduced at the cathode (negatively charged) and the strongest reducing agent is oxidized at the anode (positively charged).
- The products of electrolysis of solutions at non-standard conditions may not always be correctly predicted using the electrochemical series. For example, at high concentrations of chloride ion, the oxidation of $Cl^-(aq)$ to $Cl_2(g)$ occurs, rather than the oxidation of $H_2O(l)$ to $O_2(g)$ and $H^+(aq)$.
- The amount of material produced during electrolysis is dependent upon the charge on the ions in the electrolyte, the current being passed through the electrolysis cell and the duration of the electrolysis.
- Electroplating is an example of electrolysis.
- Electroplating refers to the application of a thin layer of one metal over another metal.

- Electroplating is used to improve the appearance or corrosion resistance of the product. In electroplating, the object to be plated forms the cathode (negative electrode) of the cell.



Chapter 8 Review questions

1 Define the term *standard electrode potential of an element*.

2 Nickel rods are placed into beakers containing 1 mol dm^{-3} solutions of $AgNO_3$, $Mg(NO_3)_2$, $Fe(NO_3)_2$, $CuSO_4$ and $Zn(NO_3)_2$ and left for several days. In which solution(s) would you expect to a coating of another metal to form on the nickel rod?

3 Strips of an unknown elemental metal are placed in three beakers containing 1 mol dm^{-3} solutions of hydrochloric acid, zinc chloride and nickel nitrate solutions. The beakers were observed over a period of one hour, and the following observations were noted.

Solution	Observations
HCl	Metal dissolved; bubbles of gas evolved
$ZnCl_2$	No reaction observed
$Ni(NO_3)_2$	Crystals form over surface of metal

a Use figure 8.1.7, p. 249 to determine the possible identity of the metal.

b Describe further measurements or experiments that could be performed to ascertain which metal was placed in the solutions.

4 Use the list of electrode potentials (figure 8.1.7 p. 249) to deduce whether or not a spontaneous reaction of any significant extent would occur in each of the following cases. Where a reaction would be expected, write the relevant half equations and the overall equation.

a Copper filings are sprinkled into a solution of silver nitrate.

b A strip of magnesium is placed into a solution of hydrochloric acid.

c Solutions of potassium bromide and zinc nitrate are mixed.

d A silver wire is placed into a solution of tin(II) chloride.

5 Use the standard electrode potentials given for the following conjugate redox pairs to answer the questions below.

Sc^{2+}/Sc $E^\ominus$ –2.12
Zn^{2+}/Zn $E^\ominus = -0.76$
Sn^{4+}/Sn^{2+} $E^\ominus = +0.15$
Ag^+/Ag $E^\ominus = +0.80$
V^{2+}/V $E^\ominus = -1.18$
Na^+/Na $E^\ominus = -2.71$

Which species is the:

a weakest oxidizing agent?

b second strongest reducing agent?

6 A student is given a beaker containing an unknown solution of $Q(NO_3)_2$ and is asked to displace metal Q from the solution. The relevant half-equation is:

$Q^{2+}(aq) + 2e^- \rightleftharpoons Q(s) \qquad E^{\ominus} = -0.55\ V$

By consulting the electrochemical series, deduce which of the metals iron, copper, zinc or lead would be suitable to perform this function.

7 A chemist made the following observations using clean metal surfaces.

- Metal B dissolved in 1 mol dm^{-3} $C(NO_3)_2$ solution, forming a deposit of metal C.
- Metal C would not dissolve in 1 mol dm^{-3} $A(NO_3)_2$ solution.
- Metal A would not dissolve in 1 mol dm^{-3} $B(NO_3)_2$ solution.

List metals A, B and C in order from the strongest reducing agent to the weakest.

8 Explain how the table of standard electrode potentials was generated. In your answer you should discuss the significance of the 'standard hydrogen half-cell' and explain what is meant by 'standard conditions'.

9 You are provided with a standard hydrogen half-cell and a solution of palladium(II) nitrate with a palladium metal electrode. Draw the electrochemical cell that you would need to construct to verify the E° for the $Pd^{2+}(aq)/Pd(s)$ conjugate pair as +0.92 V. Indicate the following, on or below your diagram:

a Anode and cathode

b Oxidation reaction and the reduction reaction

c Oxidizing agent and the reducing agent

d Polarity of each electrode

e Direction of flow of electrons through the connecting wire

f Direction of flow of ions through the KNO_3 salt bridge

g Overall balanced equation for the redox reaction

h Cell potential

10 Liquid bromine is formed when acified potassium permanganate is added to a 1 mol dm^{-3} solution of sodium bromide. Calculate the cell potential for this reaction and deduce the equation for the reaction.

11 By referring to the table of standard electrode potentials (figure 8.1.7, p. 249), name three metals that cannot be obtained by the electrolysis of their aqueous salts. Explain your reasoning.

12 A 1 mol dm^{-3} silver nitrate solution undergoes electrolysis using inert carbon electrodes. Draw a diagram of the electrolytic cell used and annotate the diagram to show the:

a polarity of the electrodes

b anode and the cathode

c oxidation and reduction reactions

d oxidizing agent and the reducing agent

e overall equation representing the cell reaction.

13 In the electrolysis of a 1 mol dm^{-3} solution of silver nitrate solution, as described in question **12**, describe the differences that would have been noted if silver electrodes had been used rather than inert carbon electrodes.

14 Consider the products of the electrolysis of a dilute solution of NaCl and a very concentrated solution of NaCl and describe the difference between the products of these two experiments.

15 Predict the products at the anode and the cathode during the electrolysis using inert electrodes of the following.

a Highly concentrated solution of sodium chloride

b 1 mol dm^{-3} sulfuric acid

c Dilute solution of calcium bromide

16 A student sets up an electrolysis cell to pass a current through a dilute solution of zinc chloride. The cell was allowed to proceed for some time and black crystals formed on one electrode and a gas was evolved from the other. A few drops of universal indicator are added to the cell near the electrodes. The colour of the indicator changes to red at the electrode where gas is being evolved, indicating that the solution is acidic. Write half-equations to explain these observations.

17 Unknown aqueous solutions were electrolysed using platinum electrodes. Suggest the identity of the solution being electrolysed, given the following products.

	Product at cathode	Product at anode	Other observations
a	Silver metal	Oxygen gas	pH around anode decreased
b	Copper metal	Iodine	
c	Hydrogen gas	Chlorine gas	pH around cathode increased

18 A student wishes to electroplate copper metal onto a locker key.

a Draw a diagram of the cell needed to achieve this aim, using the key as one electrode and a strip of copper metal as the other.

b Indicate on the diagram the pole of the power source (positive or negative) to which the key should be attached.

c State which electrode (the cathode or the anode) is the locker key.

d Explain why the concentration of Cu^{2+} ions in the electrolyte does not change.

e Suggest a suitable electrolyte for this cell.

f Describe how the student might remove the copper from the key.

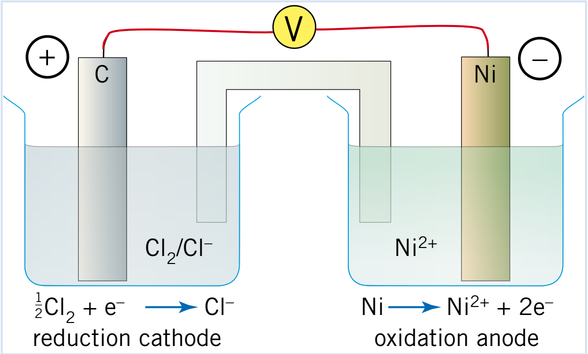
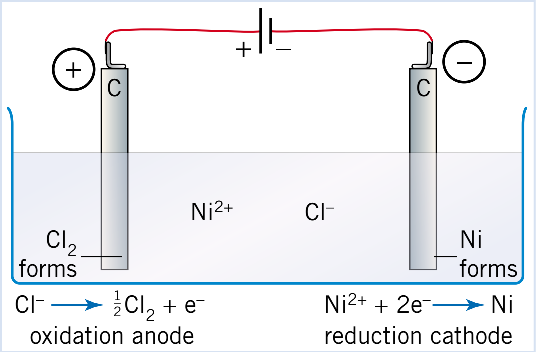
19 In an experiment involving the electrolysis of molten potassium bromide, 0.5 mol of bromine was formed.

a State the equation for the formation of bromine during electrolysis.

b Deduce, giving a reason, the amount of potassium formed at the same time.

c Discuss other factors that affect the amount of product formed during electrolysis.

20 Chlorine gas and nickel metal will react spontaneously, but an external power supply is required to induce a reaction between nickel ions and chloride ions. Copy and complete the table below.

Chlorine and nickel voltaic cell	**Chloride ions and nickel ions electrolytic cell**
	
Half-equations: Oxidation at the ___________ (–) $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ ____________ at the cathode (+) $\frac{1}{2}Cl_2(aq) + e^- \rightarrow Cl^-(aq)$ ___________	**Half-equations:** __________ at the anode (+) $Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$ Reduction at the ___________ (–) $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$
Overall equation: ___________ → __________	**Overall equation:** _________ → __________
Products: Nickel ions and chloride ions Salt bridge required, _________ energy converted to _________ energy Separate half-cells	**Products:** Nickel metal and chlorine gas Power supply required, electrical energy converted to ___________ energy Single cell only

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Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 8 Test

Part A: Multiple-choice questions

1 The standard electrode potentials for Al and Mn are given below:

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad -1.66\ V$

$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s) \quad -1.18\ V$

What is the potential of a cell prepared with these metals in contact with 1.0 mol dm^{-3} solutions of their ions?

A 0.22 V

B 0.48 V

C 2.84 V

D 3.43 V

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2 Which factor does **not** affect the value of the standard electrode potential of a half-cell?

A The surface area of the electrode

B The concentration of the solution

C The temperature of the solution

D The material of the electrode

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3 The mass of a metal deposited during electrolysis does **not** depend on:

A the current flowing

B the voltage between the electrodes

C the time for which the current passes

D the charge on the metal ion

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4 Which pair of factors both affect the amount (in mol) of chlorine produced in the electrolysis of aqueous sodium chloride?

A Current and temperature

B Temperature and chloride ion concentration

C Chloride ion concentration and length of time of electrolysis

D Pressure and length of time of electrolysis

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5 Which one of the following could reduce $Cr_2O_7^{2-}(aq)$ to $Cr^{3+}(aq)$?

A $Ca^{2+}(aq)$

B $Cu^{2+}(aq)$

C $Fe^{2+}(aq)$

D $Zn^{2+}(aq)$

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6 $Tl^+(aq) + e^- \rightarrow Tl(s) \quad E^\ominus = -0.336\ V$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad E^\ominus = 0.339\ V$

The standard electrode potentials for two metals are given above. What are the equation and cell potential for the spontaneous reaction that occurs?

A $Tl^+(aq) + Cu^{2+}(aq) \rightarrow Tl(s) + Cu(s) \quad E^\ominus = 0.003\ V$

B $2Tl(s) + Cu^{2+}(aq) \rightarrow 2Tl^+(aq) + Cu(s) \quad E^\ominus = 0.675\ V$

C $2Tl(s) + Cu^{2+}(aq) \rightarrow 2Tl^+aq) + Cu(s) \quad E^\ominus = 1.011\ V$

D $2Tl^+(aq) + Cu(s) \rightarrow 2Tl(s) + Cu^{2+}(aq) \quad E^\ominus = 0.333\ V$

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7 Which is a feature of the standard hydrogen electrode?

A Hydrogen gas at 1.01×10^5 Pa (1 atm) pressure

B 1.0 mol dm^{-3} sulfuric acid

C A temperature of 273 K

D A magnesium electrode

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8 Aqueous solutions containing different concentrations of NaCl were electrolysed using platinum electrodes. What is the **major** product at the positive electrode in each case?

	0.001 mol dm^{-3} NaCl(aq)	1.0 mol dm^{-3} NaCl(aq)
A	H_2	Na
B	H_2	H_2
C	O_2	Cl_2
D	Cl_2	O_2

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9 The standard electrode potentials of three elements are as follows:

X +1.09 V

Y +0.54 V

Z +1.36 V

Which statement is correct?

A Z will oxidize Y^-(aq) and X^-(aq).

B Y will oxidize X^-(aq) and Z^-(aq).

C X will oxidize Y^-(aq) and Z^-(aq).

D Z will oxidize Y^-(aq) but not X^-(aq).

© IBO HL Paper 1 Nov 02 Q33

10 Which statement is correct?

A Spontaneous redox reactions produce electricity in an electrolytic cell.

B Electricity is used to carry out a non-spontaneous redox reaction in a voltaic cell.

C Oxidation takes place at the negative electrode in a voltaic cell and the positive electrode in an electrolytic cell.

D Oxidation takes place at the negative electrode in a voltaic cell and reduction takes place at the positive electrode in an electrolytic cell.

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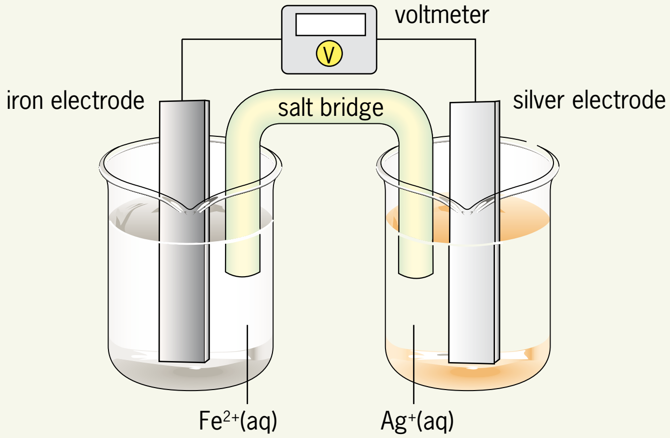
(10 marks)

Web Destinations www.pearsoned.com.au/schools

For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

Part B: Short-answer questions

1 The following diagram shows a voltaic cell.



a State an equation to represent the spontaneous reaction occurring in the cell.

(1 mark)

b Define the term *standard electrode potential*.

(1 mark)

c Use Appendix 6 to calculate the standard cell potential for the spontaneous reaction in part **a**.

(1 mark)

d Draw arrows on the (bottom left) diagram to indicate the direction of electron flow.

(1 mark)

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2 A blue aqueous solution of copper(II) sulfate, $CuSO_4$, is electrolysed using copper electrodes.

a Write balanced half-equations, with state symbols, for the reactions occurring at the:

anode (positive electrode)

(1 mark)

cathode (negative electrode)

(1 mark)

b State whether or not the colour of the solution will change as the electrolysis proceeds. Explain your answer.

(1 mark)

c Write a balanced chemical equation for the products formed if the copper anode is replaced by a graphite anode.

(2 marks)

d State whether or not the colour intensity and pH of the solution will change as the electrolysis proceeds in part **c** above.

(2 marks)

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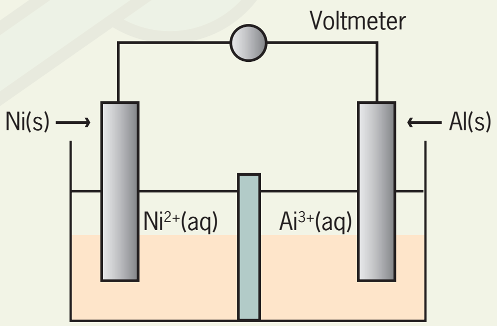
3 **a** In the following representation of a cell, label each electrode with a + or a – sign, as appropriate, and draw an arrow on the connecting wire to indicate the direction of electron flow. (Refer to Appendix 6.)

(1 mark)



b **i** Write the balanced equation for the spontaneous reaction in the above cell.
(2 marks)

ii Calculate the standard cell potential.
(2 marks)

© IBO HL Paper 2 May 00 Q4b, c

Part C: Data-based question

The following are standard electrode potentials.

Half-equation	$E^\ominus$ / V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77

a These values were obtained using a standard hydrogen electrode. Describe the materials and conditions used in the standard hydrogen electrode. (A suitably labelled diagram is acceptable.)
(5 marks)

b Define the term *oxidizing agent* in terms of electron transfer, and identify the strongest oxidizing agent in the list above.
(2 marks)

c A cell was set up using zinc in zinc sulfate solution and copper in copper(II) sulfate solution, both solutions being under standard conditions.

i Calculate the cell potential.
(1 mark)

ii Write an equation for the spontaneous cell reaction.
(2 marks)

d Both zinc and tin are used to coat iron to prevent it from rusting. Once the surface is scratched, oxygen and water containing dissolved ions come into contact with the iron and the coating metal.

Explain why electrolysis of aqueous zinc sulfate may not be used for coating with zinc metal.
(2 marks)

© IBO HL Paper 2 Nov 04 Q9a–c, d(iii)

Part D: Extended-response question

Some standard electrode potentials are shown in Appendix 6.

a Using information from the table, determine whether or not there is a spontaneous reaction between copper metal and a solution containing hydrogen ions.
(2 marks)

b Using information from the table, identify a substance that will oxidize bromide ions but not chloride ions. Explain your choice, and write an equation for the redox reaction you have chosen.
(5 marks)

c Sodium chloride in aqueous solution is electrolysed.

i Identify the substances formed, and their relative amounts, when a concentrated solution is used.
(2 marks)

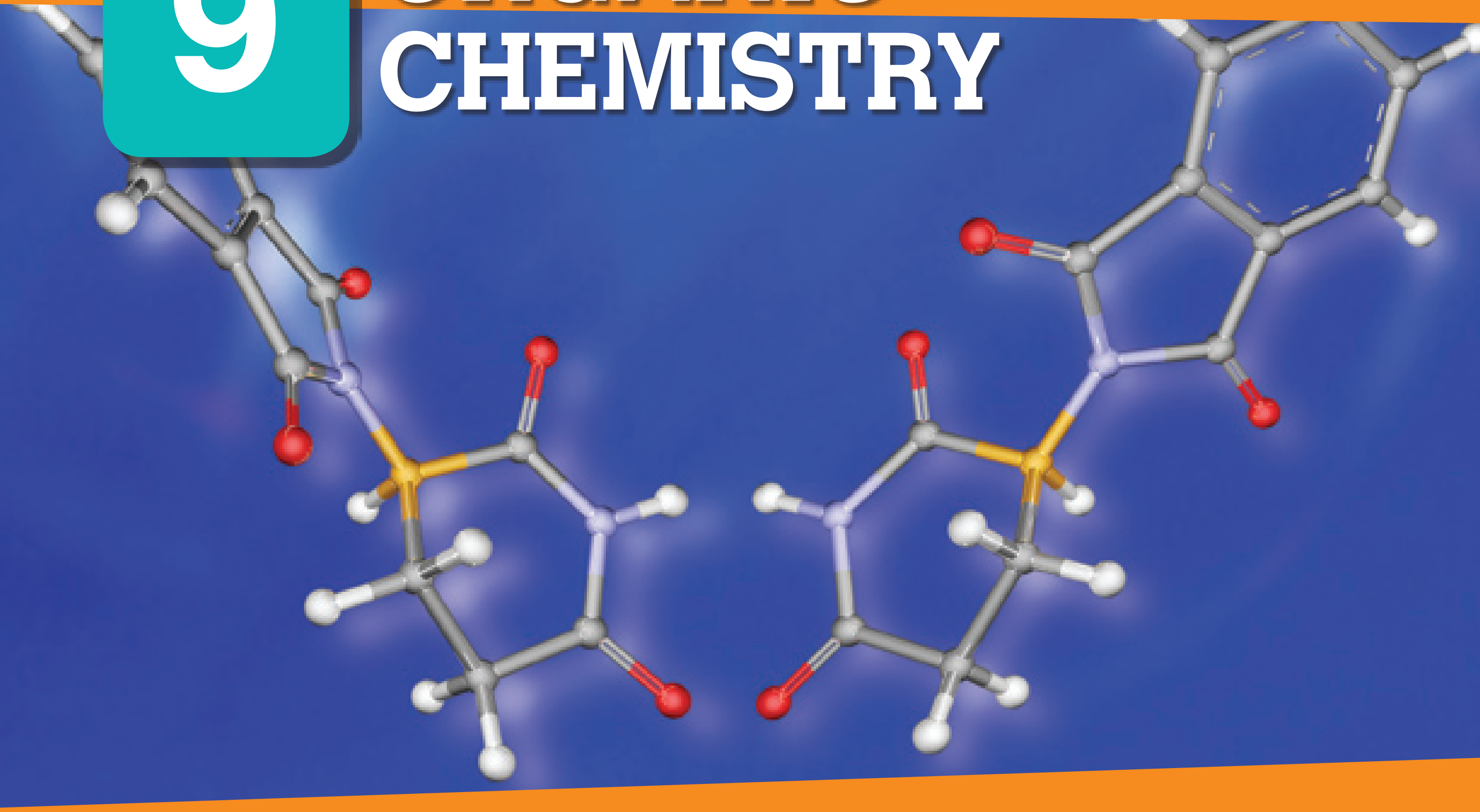
ii Identify the substances formed, and their relative amounts, when a very dilute solution is used.
(2 marks)

iii Write an equation for a reaction occurring when aqueous sodium chloride, but not molten sodium chloride, is electrolysed.
(1 mark)

© IBO HL Paper 2 Nov 04 Q10b, c, e
Total marks: 50

9

ORGANIC CHEMISTRY



Chapter overview

This chapter covers the IB Chemistry syllabus Topic 20: Organic Chemistry.

By the end of this chapter, you should be able to:

- deduce structural formulas for compounds of the functional groups: amine, amide, ester and nitrile up to C_6
- recognize and name (using the IUPAC system) amines, amides, esters and nitriles up to C_6
- describe, using equations, substitution reactions of halogenoalkanes with ammonia and potassium cyanide
- describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst
- write the S_N2 mechanism for the reactions of primary halogenoalkanes with ammonia and potassium cyanide
- describe and explain how the rate of nucleophilic substitution reactions in halogenoalkanes depends on the identity of the nucleophile, the identity of the halogen and the nature (primary, secondary or tertiary) of the halogenoalkane
- describe using equations, the elimination of HBr from bromoalkanes
- describe and explain the mechanism for the elimination of HBr from bromoalkanes
- describe, using equations, the reactions of carboxylic acid with alcohols and amines
- state the uses of esters
- deduce the structures of polymers formed by the reactions of carboxylic acids with alcohols and amines
- identify the repeating unit in condensation polymers
- outline the economic importance of condensation reactions
- construct organic reaction pathways for the production of a range of organic compounds given the starting materials and the product
- distinguish between structural isomers and stereoisomers
- describe and explain geometric isomerism in non-cyclic alkenes and cycloalkanes (up to C_4)
- explain differences in physical and chemical properties of geometric isomers
- describe and explain optical isomerism in simple molecules
- outline the use of a polarimeter to distinguish between optical isomers
- compare the physical and chemical properties of optical isomers.

IBO Assessment statements 20.1.1 to 20.6.7

The diversity of life owes much to the diverse chemistry of one element—carbon. More than 90% of known compounds contain carbon, and there can be little doubt as to the importance of the study of organic chemistry, the chemistry of carbon. We have seen in the Standard Level course that the study of the millions of known organic compounds is simplified by studying the structures and reactions of homologous series of compounds containing particular functional groups. We have also seen that the study of organic compounds is somewhat complicated by the existence of isomers, compounds that are the 'same' but not 'identical'. In this chapter we will consider more functional groups and their reactions, and more types of isomerism. We will also look closely at how certain organic reactions occur and at the mechanism of these reactions, and begin to see how an understanding of reaction mechanisms allows us to choose conditions to favour the synthesis of desired organic compounds.

AS **20.1.1**
Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. © IBO 2007

AS **20.1.2**
Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. © IBO 2007

9.1 MORE FUNCTIONAL GROUPS

We saw in the Standard Level course that a functional group is an atom or group of atoms attached to a hydrocarbon chain. These functional groups are significant because, to a large extent, they determine the reactivity and chemical properties of the compound. **Homologous series** containing functional groups encountered earlier in the course are shown in table 9.1.1. To this list of functional groups we will now add amines, nitriles, esters and amides.

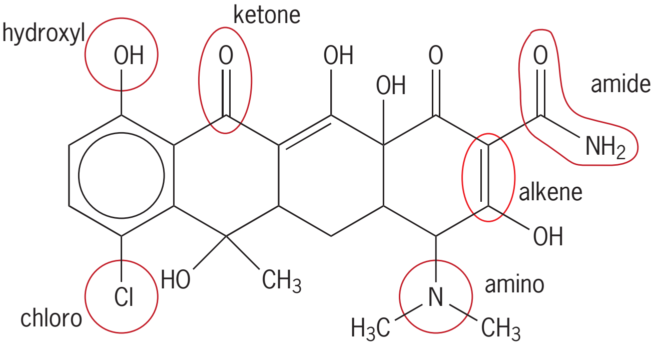
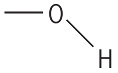
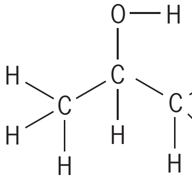
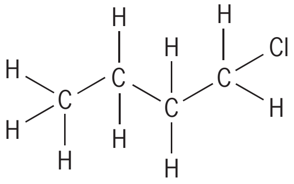
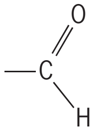
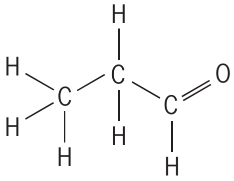
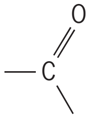
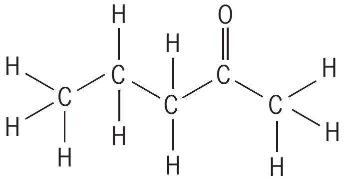
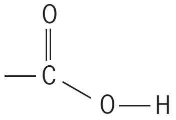
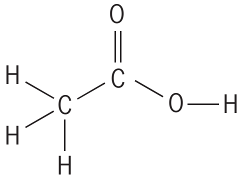


Figure 9.1.1 A molecule of the antibiotic chlortetracycline contains several different functional groups.

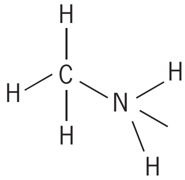
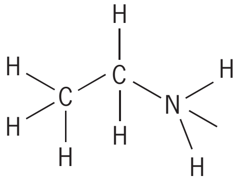
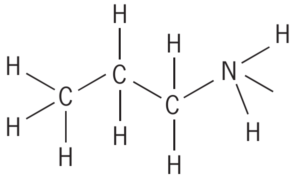
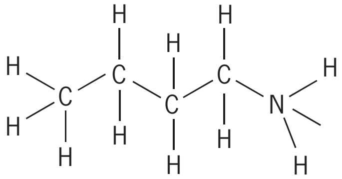
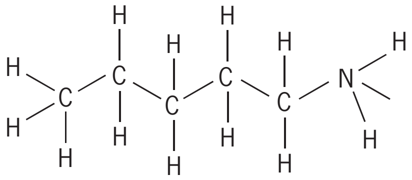
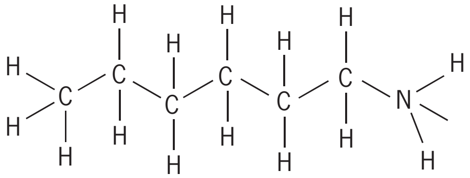
TABLE 9.1.1 FUNCTIONAL GROUPS

Homologous series	Structural formula	Condensed structural formula	Suffix or prefix used in naming	Example
Alcohols		R–OH	-ol	 2-propanol
Halogenoalkanes	—X	R–X	halo, e.g. chloro-	 1-chlorobutane
Aldehydes		R–CHO	-al	 propanal
Ketones		R–COR′	-one	 pentan-2-one
Carboxylic acids		R–COOH	-oic acid	 ethanoic acid

Amines

The **amine** functional group is made up of a nitrogen atom bonded to two hydrogen atoms. This $–NH_2$ group is known as an amino group and replaces one hydrogen in the structure of an alkane. Amines are generally named using the prefix amino-, with a number used to indicate the location of the $–NH_2$ group. The suffix -amine may also be used. In addition, for simpler amines the suffix -ylamine, an older system of naming, is also used. Thus the compound with semi-structural or condensed formula $CH_3CH_2CH_2NH_2$ may be named 1-aminopropane, 1-propanamine or 1-propylamine.

TABLE 9.1.2 THE FIRST SIX MEMBERS OF THE STRAIGHT-CHAIN PRIMARY AMINE SERIES

Name	Condensed structural formula	Structural formula	Boiling point (°C)
Methanamine Methylamine	CH_3NH_2		–6
Ethanamine Ethylamine	$C_2H_5NH_2$		17
1-Propanamine 1-Propylamine	$C_3H_7NH_2$		49
1-Butanamine 1-Butylamine	$C_4H_9NH_2$		78
1-Pentanamine	$C_5H_{11}NH_2$		104
1-Hexanamine	$C_6H_{13}NH_2$		133

Substitution of one or both of the hydrogens in the $–NH_2$ group with alkyl groups produces secondary or tertiary amines, depending on the number of alkyl groups attached to the nitrogen atom. In secondary amines, RR′NH, the main part of the name comes from the largest carbon chain attached to the nitrogen atom. The other carbon chain is prefixed as an alkyl group, with the location prefix given as an italic *N* (as it is attached to the nitrogen, N, atom). Examples include *N*-ethylpropanamine and *N*-methylethanamine. For tertiary amines RR′R″N, two italic *N* prefixes are used, as illustrated by the name *N*,*N*-dimethylpropanamine. Figure 9.1.2 shows examples of the three types of amines, along with their semi-structural formulas and systematic names.

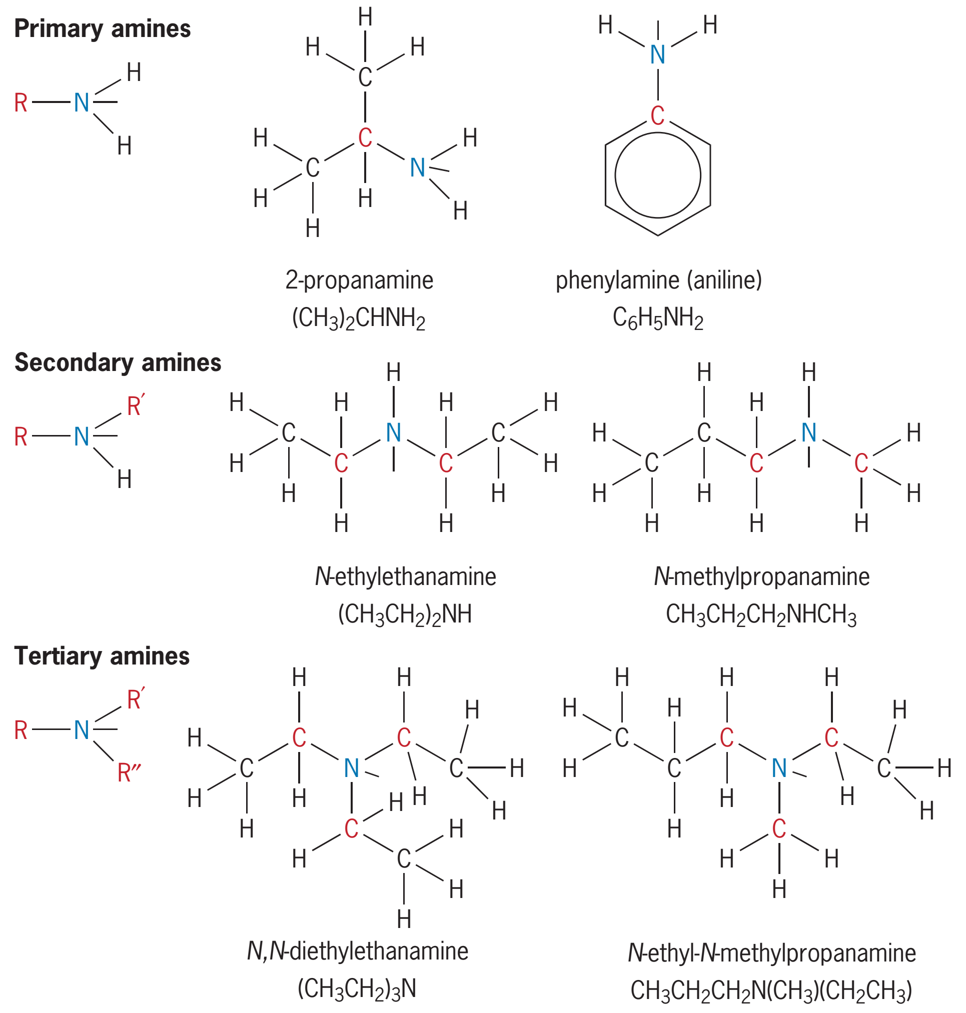


Figure 9.1.2 Examples of primary, secondary and tertiary amines.

Although the amine group is normally found associated with other functional groups, some free amines do exist. Dimethylamine ($(CH_3)_2NH$) and trimethylamine ($(CH_3)_3N$) are found in rotting fish, and putrescine ($NH_2(CH_2)_4NH_2$) and cadaverine ($NH_2(CH_2)_5NH_2$) are found in rotting flesh. The peculiar smell of decaying animal flesh is partly due to these amines. The amine group is widespread in biological molecules, including proteins.

Amines are closely related to ammonia, NH_3, and many of their properties are similar to those of ammonia. Like ammonia, the smaller amines are gaseous and highly soluble in water. This solubility is due to hydrogen bonding between the highly polar NH_2 group and water molecules. This polarity also leads to amines having higher boiling points than non-polar compounds of similar molar mass, but lower boiling points than alcohols and carboxylic acids of comparable mass. Like ammonia, the primary amines are basic, being able to accept a proton to form the amine cation, $R–NH_3^+$. For example, ethanamine is readily soluble in water, and reacts slightly with water to form an alkaline solution containing the $CH_3CH_2NH_3^+$ cation. Reaction is only partial as the amine is a weak base.

$$CH_3CH_2NH_2(g) + H_2O(l) \rightleftharpoons CH_3CH_2NH_3^+(aq) + OH^-(aq)$$

Like ammonia, the three amine classes all have a non-bonding pair of electrons on the nitrogen atom. The tendency of nitrogen to share this pair of electrons accounts for the chemical behaviour of amines—their basicity and, as we will see later, their action as nucleophiles.

CHEM COMPLEMENT

Molecules that really smell bad!

Like ammonia, many amines have an unpleasant smell; however, there are three amines that are famous for their terrible smell. Skatole (3-methylindole) is a component of faeces. It is a secondary amine that dissolves in hot water and gives a characteristic faecal smell. The smell of putrescine could be described as 'the smell of death'. Both putrescine and cadaverine are found in putrefying and rotting flesh, since they are the breakdown products of some of the amino acids found in animals. These primary amines may also be produced by living animals, but as they are poisonous, they are excreted as quickly as possible by the body. For example, the odour of bad breath and urine are 'enriched' by the presence of these molecules. Bacterial infections of the vagina may be identified when potassium hydroxide is added to a sample of vaginal secretions and a doctor has the unpleasant task of determining the presence of cadaverine and putrescine by a 'whiff' test!

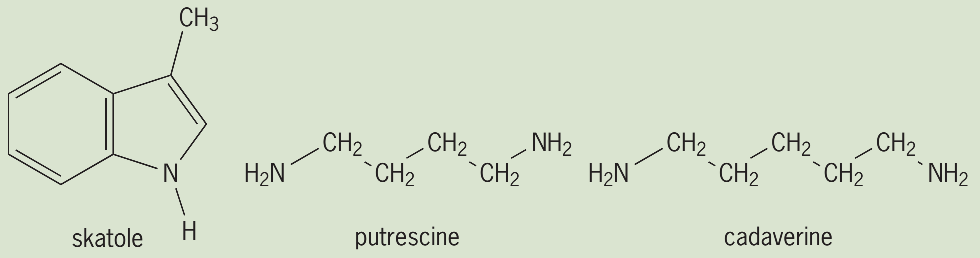


Figure 9.1.3 Structures of skatole, putrescine and cadaverine.

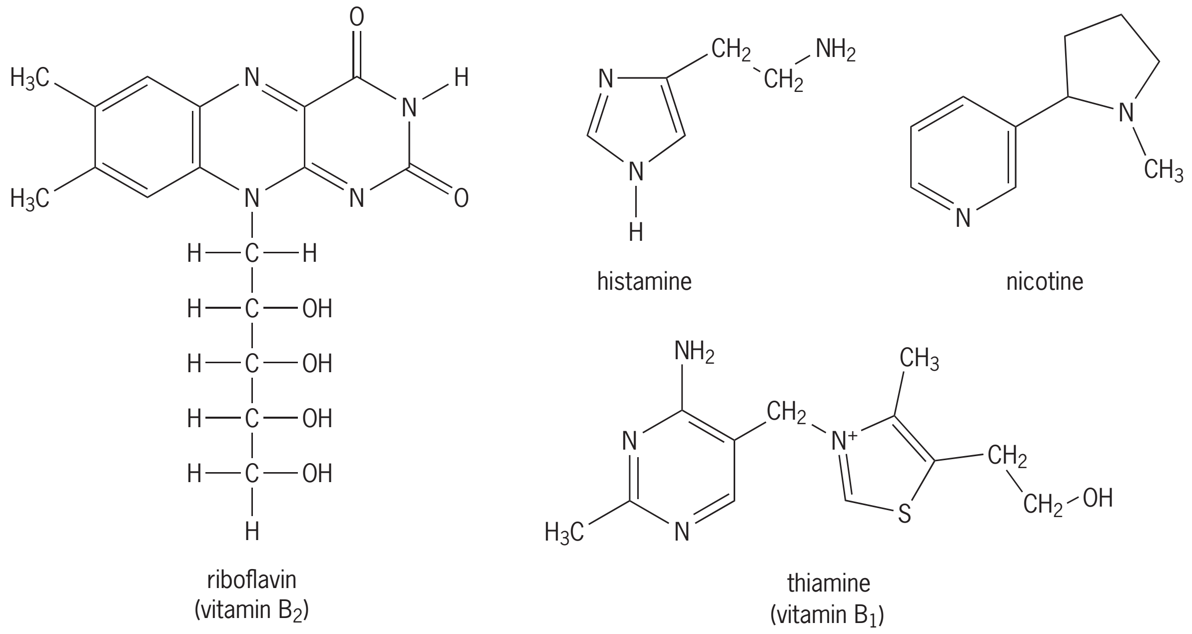


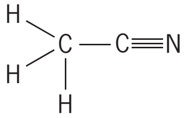
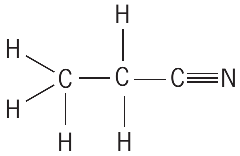
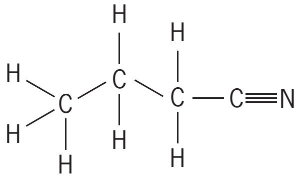
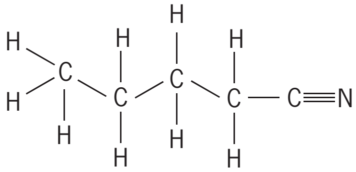
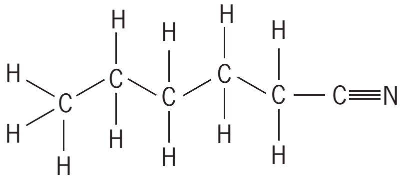
Figure 9.1.4 Naturally occurring amines found in plants and animals.

Nitriles

The **nitrile** functional group is made up of a carbon atom triple bonded to a nitrogen atom. Although sometimes called cyanides or cyano compounds, nitriles are systematically named using the nitrile suffix. The stem indicates the number of carbon atoms, including that in the –CN group. For example, CH_3CN is ethanenitrile. The smaller nitriles are liquids with a sweet smell, and are very soluble in water.

Figure 9.1.5 Nitriles are used in the production of some synthetic rubber gloves suitable for use by those with sensitivities to natural latex rubber.

TABLE 9.1.3 THE FIRST FIVE MEMBERS OF THE NITRILE SERIES

Name	Condensed structural formula	Structural formula	Boiling point (°C)
Ethanenitrile	CH_3CN		82
Propanenitrile	C_2H_5CN		97
Butanenitrile	C_3H_7CN		118
Pentanenitrile (valeronitrile)	C_4H_9CN		139–141
Hexanenitrile (capronitrile)	$C_5H_{11}CN$		161–164

Esters

The ester functional group contains a carbonyl group with a second oxygen atom bonded to the carbon. It is usually represented as R–COO–R′. Notice that the ester functional group is found in the middle of the molecule. Esters are one of the most widespread of all naturally occurring compounds. Many have characteristic sweet odours, and are often responsible for the fragrance of fruits and flowers. Esters are often used in the preparation of artificial flavours and perfumes. They are also widely used in chemical industries. Ethyl ethanoate is a common solvent. The ester functional group is present in animal fats and plant oils, and is also found in many biologically important molecules.

Figure 9.1.6 Esters are responsible for the pleasant tastes and odours of many fruits.

Esters are given two part names obtained from the acid and alcohol from which they are prepared (we will consider this ester-producing reaction on page 308). First, the alkyl group attached to the oxygen atom is identified and used as the name prefix. This alkyl group is derived from the alcohol. The carboxylic acid group is then named, with the -oic ending replaced by -oate. Thus $CH_3CH_2COOCH_2CH_3$ is named ethyl propanoate.

Esters have no free hydroxyl groups, so they cannot form hydrogen bonds with each other. They are therefore more volatile (have lower boiling points) than acids and alcohols of similar molar mass. Esters have similar boiling points to aldehydes and ketones of comparable molar mass.

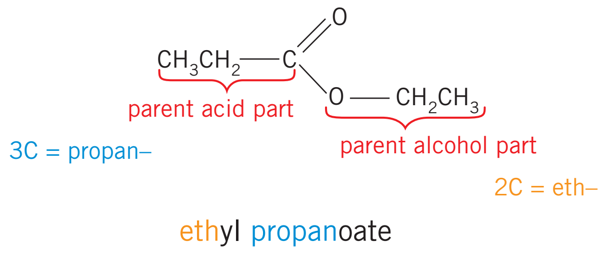
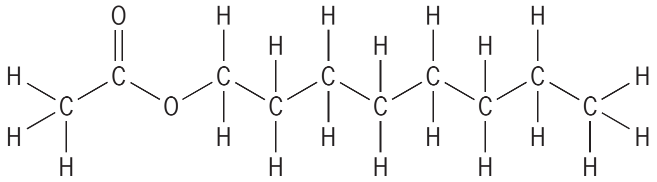
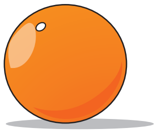
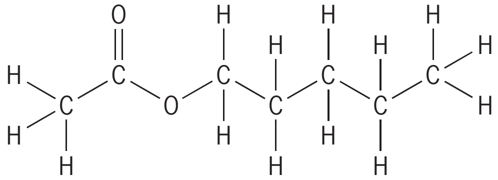
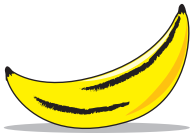
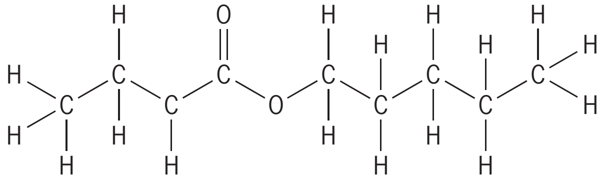
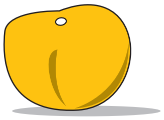
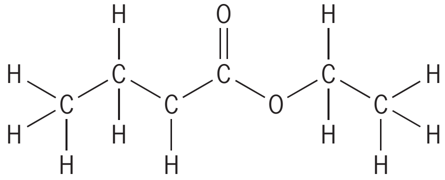
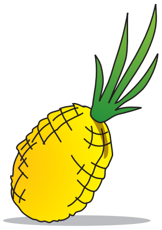


Figure 9.1.7 Esters are named using the parent alcohol and acid names.

TABLE 9.1.4 ESTERS AND THEIR ODOURS

Name	Structural formula	Odour
Octyl ethanoate		orange 
Pentyl ethanoate		banana 
Pentyl butanoate		apricot 
Ethyl butanoate		pineapple 

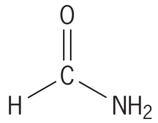
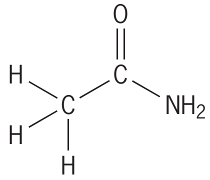
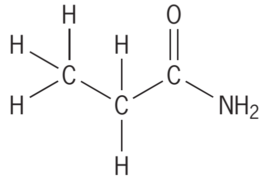
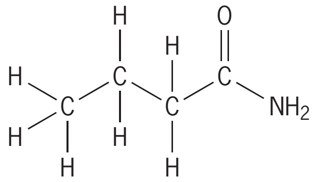
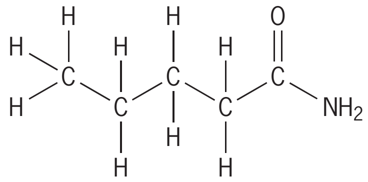
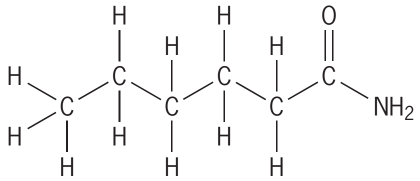
Amides

The **amide** functional group can be considered as a derivative of the carboxylic acid group in which the –OH of the carboxyl group is replaced by –NH_2. The amide group is represented as R–$CONH_2$. This group is a key functional group in the structure of proteins and some important polymers (see pages 311–313). Amides are polar, and so are capable of strong intermolecular hydrogen bonding. This gives them quite high boiling points. The smaller members of the group, with up to six carbons, are soluble in water.

Amides are named by changing the -oic acid ending of the name of the corresponding carboxylic acid to amide. For example, CH_3CH_2COOH, propanoic acid, becomes $CH_3CH_2CONH_2$, propanamide. Substituted amides are named using this system, but adding a prefix of *N*-alkyl or *N*,*N*-dialkyl. For example, $CH_3CH_2CONHCH_3$ is *N*-methylpropanamide, and $CH_3CON(CH_3)_2$ is *N*,*N*-dimethylethanamide (see figure 9.1.8).

WORKSHEET 9.1
Functional groups

TABLE 9.1.5 **THE FIRST SIX MEMBERS OF THE AMIDE SERIES**

Name	Condensed structural formula	Structural formula	Boiling point (°C)
Methanamide	$HCONH_2$		220
Ethanamide	CH_3CONH_2		221
Propanamide	$C_2H_5CONH_2$		213
Butanamide	$C_3H_7CONH_2$		216
Pentanamide	$C_4H_9CONH_2$		225
Hexanamide	$C_5H_{11}CONH_2$		255

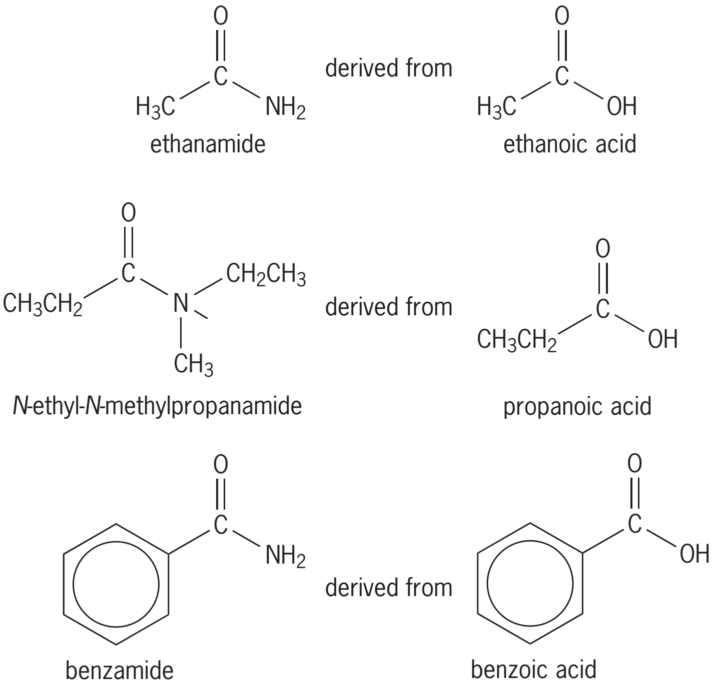
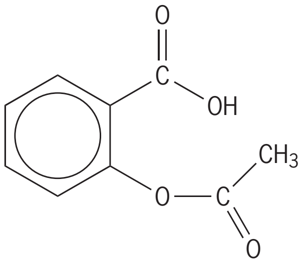


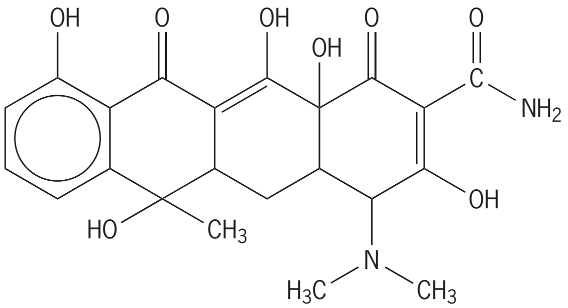
Figure 9.1.8 Amides are named after their corresponding carboxylic acids.

Section 9.1 Exercises

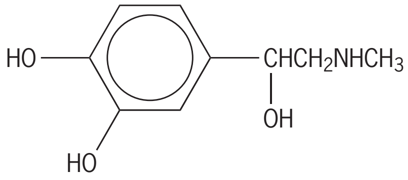
1 The structures of several drug molecules are shown below.



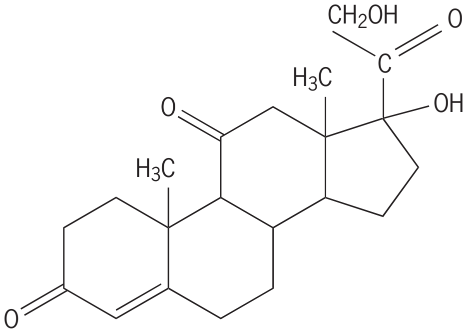
aspirin



tetracycline



epinephrine



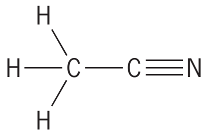
cortisone

Name one drug molecule that contains:

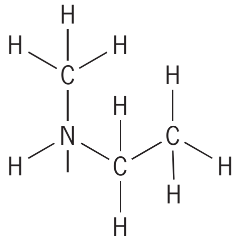
- **a** an amide group
- **b** an ester group
- **c** a carboxylic acid group
- **d** a secondary amine group
- **e** a ketone

2 Name each of the compounds whose structural formulas are shown below.

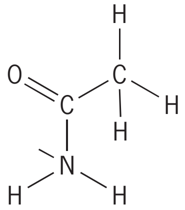
a



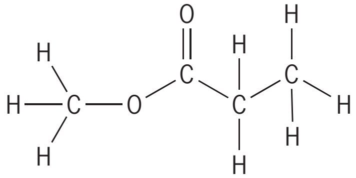
b



c



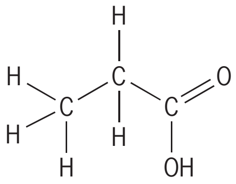
d



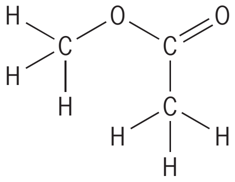
3 Name each of the compounds whose semi-structural formulas are shown below.

- **a** $CH_3CH_2COOCH_2CH_3$
- **b** $CH_3CONHCH_3$
- **c** $(CH_3)_3N$
- **d** $CH_3CH_2CH_2CN$

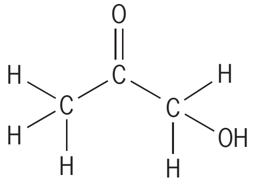
4 Four molecules, all with the formula $C_3H_6O_2$, are shown below.



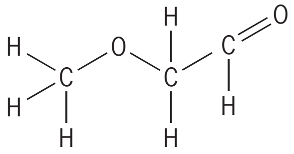
I



II



III



IV

- **a** What is the name given to molecules such as these, which differ in structure but have the same molecular formula?
- **b** Circle and name all the functional groups in each of the four molecules.

5 Draw structural formulas for a compound of molecular formula C_3H_7NO that contains:

- **a** an aldehyde and a secondary amine
- **b** a ketone and a primary amine
- **c** an amide.

6 Draw structural formulas for a compound of molecular formula $C_4H_8O_2$ that contains:

- **a** an ester
- **b** a carboxylic acid
- **c** a ketone and an alcohol.

7 Draw structural formulas, and give the names of, three:
   a amines of formula C_3H_9N
   b amides of formula C_3H_7NO.

8 Ethanoic acid and methyl methanoate both have the molecular formula $C_2H_4O_2$. Which compound would be expected to have the higher boiling point? Explain your choice.

9.2 REACTIONS INVOLVING AMINES AND NITRILES

Synthesis of amines

AS 20.2.4
Describe, using equations, the substitution reactions of halogenoalkanes with ammonia and potassium cyanide. © IBO 2007

Synthesis of amines may be carried out by reacting a halogenoalkane with ammonia. Reaction between the halogenoalkane and a concentrated ammonia solution is carried out by heating the reactants under pressure, or allowing them to stand together at room temperature. The use of excess ammonia increases the yield of the amine.

$$RX + NH_3 \rightarrow RNH_2 + HX$$

Reaction involves the substitution of the halogen atom, X, with the amino functional group, $-NH_2$. Recall from the Standard Level course that this type of reaction is known as a **nucleophilic substitution**. In halogenoalkanes the difference in electronegativity of the carbon and halogen atoms leads to significant bond polarity. The carbon therefore carries a slight positive charge and so is susceptible to attack by an electron-rich atom or group of atoms. Such an atom or group of atoms is known as a **nucleophile** (meaning *nucleus loving*). The attacking nucleophile displaces the halogen atom. In amine synthesis, the ammonia molecule, with its non-bonding electron pair on the nitrogen, acts as the attacking nucleophile, seeking out the positive charge on the carbon atom of the halogenoalkane. The halogen is displaced, as the amino group becomes attached to the carbon atom of the alkane stem. A hydrogen halide is produced as the second product. This reaction is shown in figure 9.2.1, in which curly arrows (shown here in green) are used to represent the movement of electron pairs.

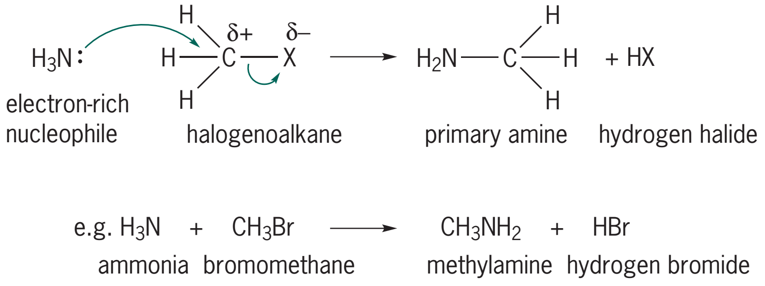


Figure 9.2.1 Nucleophilic substitution of a halogenoalkane to produce an amine.

A disadvantage of this method of amine synthesis is that the reaction produces various types of amine products—the reaction does not stop with the primary amine! A sequence of reactions occurs because the primary amine is itself a nucleophile, and can react with the halogenoalkane to produce a secondary amine. This in turn is also a nucleophile, reacting to produce a tertiary amine.

For this reason the yield of the primary amine is low, and this type of reaction is not favoured for synthesis of primary amines.

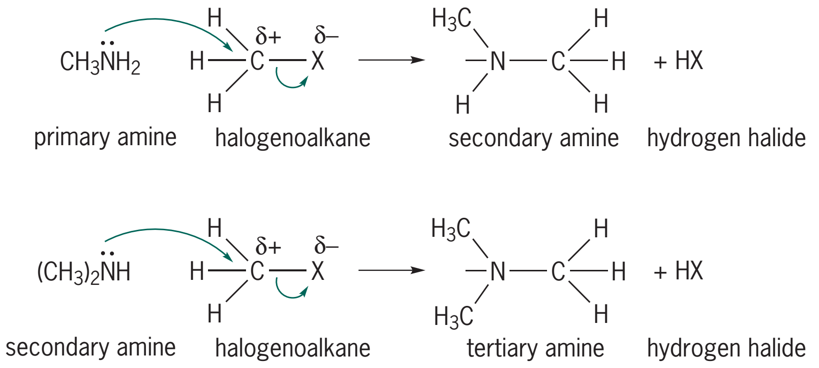


Figure 9.2.2 The nucleophilic substitution reaction of a halogenoalkane with ammonia produces a range of amine products.

AS 20.2.5
Explain the reactions of primary halogenoalkanes with ammonia and potassium cyanide in terms of the S_N2 mechanism. © IBO 2007

What is the mechanism of the substitution reaction to produce amines? Recall from the Standard Level course that nucleophilic substitution occurs by two mechanisms: **S_N1 unimolecular nucleophilic substitution reaction**, and **S_N2 bimolecular nucleophilic substitution reaction**. For primary halogenoalkanes, S_N2 is the favoured reaction mechanism. This reaction displays second-order kinetics, and the rate of reaction depends on the concentration of both reactants.

$$\text{Rate} = k[\text{nucleophile}][\text{RX}].$$

Reaction involves a single step. The nucleophile (Nu) attacks the central carbon atom from the direction opposite the halogen atom, leading to a transition state with a partly formed C–Nu bond and a partially broken C–X bond. A new product is formed with the departure of the halogen ion (X^-). Note that in figure 9.2.3 the molecular structures are shown in considerable detail. To help visualize these three-dimensional molecules using a two-dimensional representations, dashed lines are used for bonds pointing behind the page, and wedge-shaped lines for bonds pointing out of the page. We will use this method of representation to try to view clearly the progress of the reaction.

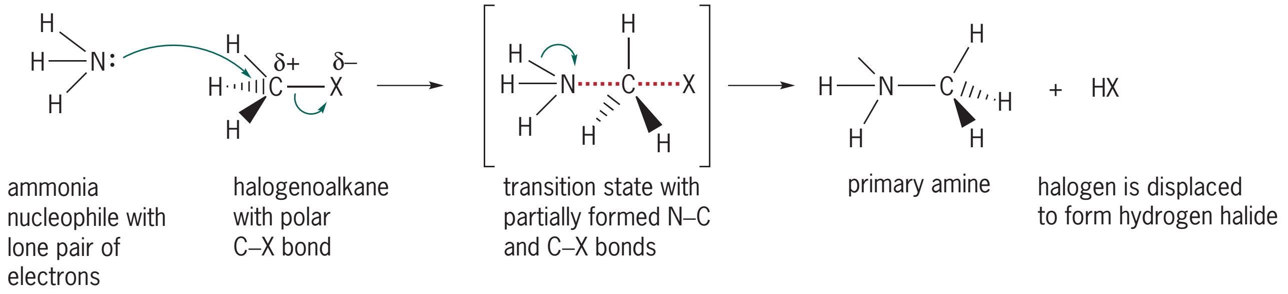


Figure 9.2.3 Primary halogenoalkanes react to form amines by bimolecular nucleophilic substitution reaction, S_N2.

Synthesis of nitriles

Like amines, nitriles may be prepared by a nucleophilic substitution of a halogenoalkane. The halogenoalkane R–X is mixed with potassium cyanide, KCN, in a solvent (such as dimethylsulfoxide, $(CH_3)_2SO_3$) that will dissolve both reactants. Reaction is rapid and exothermic. The cyanide ion, CN^-, acts as a nucleophile in an S_N2-type reaction. In the transition state, the C–C bond is partially formed and the C–X bond is partially broken. The nitrile is formed as the halogen ion (X^-) is expelled.

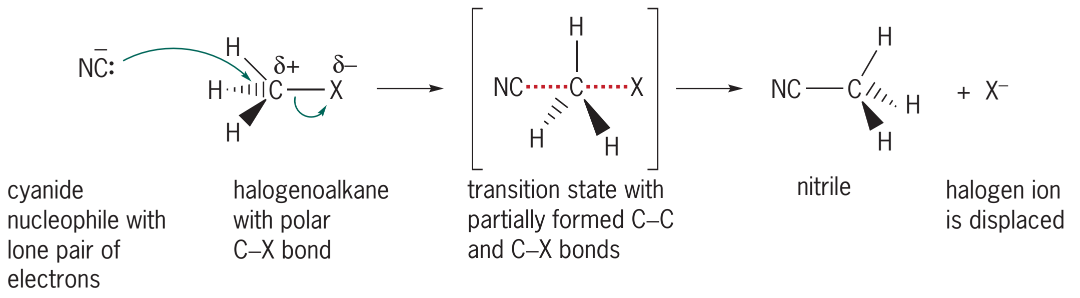


Figure 9.2.4 Primary halogenoalkanes react to form nitriles by bimolecular nucleophilic substitution reaction, S_N2.

This method of synthesis occurs for primary halogenoalkanes to form RCH_2CN products. This reaction again highlights the importance of nucleophilic substitutions of halogenoalkanes in organic syntheses. The halogen is replaced by the cyano functional group, leading to an increase in the carbon chain length by one carbon atom.

Reactions of nitriles

AS 20.2.6
Describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst.
© IBO 2007

Nitriles are an important synthetic molecule. They may be used to prepare carboxylic acids by hydrolysis (reaction with water).

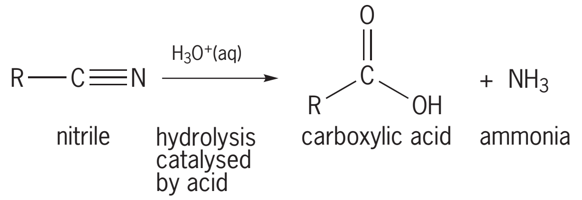


Figure 9.2.5 Nitriles may be reacted to form carboxylic acids.

They may also be used to prepare amines by reduction with hydrogen and a nickel catalyst. Recall that the addition of hydrogen to a compound is a reduction process.

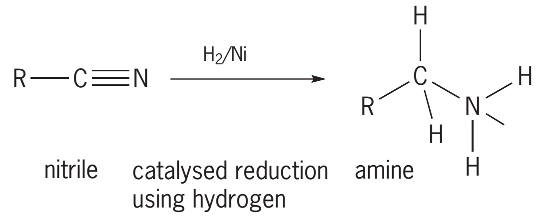


Figure 9.2.6 Nitriles may be reduced to form amines.

Notice that the synthetic pathway that converts a halogenoalkane into a nitrile, which is then reduced to an amine, results in the product having one more carbon atom than the starting reagent.

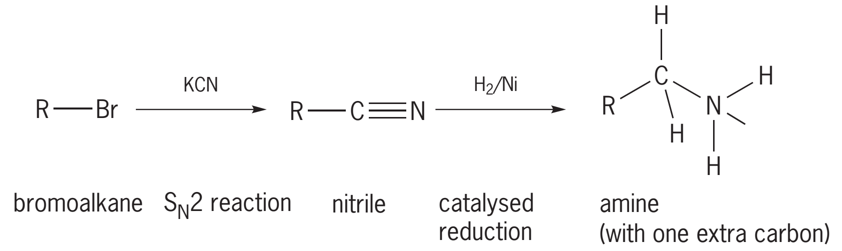


Figure 9.2.7 Nitriles provide a means in a reaction pathway of lengthening the carbon chain by one carbon atom.

Section 9.2 Exercises

1 **a** Define the term *nucleophile*.

b Name two nucleophiles other than the cyanide ion and ammonia.

2 State what the 2 refers to in an S_N2 reaction.

3 Write semi-structural or condensed formulas for the products expected from the S_N2 reaction of 1-bromobutane with:

a NaOH

b NH_3

c KCN

4 Draw a reaction mechanism diagram (using curly arrows to represent the movement of electron pairs) to show the reaction of 1-bromoethane with ammonia to form ethylamine by an S_N2 reaction.

5 Why is the reaction described in question **4** generally not used for any large-scale synthesis of ethylamine?

6 **a** Draw a reaction mechanism diagram (using curly arrows to represent the movement of electron pairs) to show the reaction of 2-bromopropane with ammonia by an S_N2 reaction.

b Name the organic product of the reaction in part **a**.

7 Draw a reaction mechanism diagram (using curly arrows to represent the movement of electron pairs) to show the reaction of 1-bromoethane with potassium cyanide to form propanenitrile.

8 Would you expect chloromethane or iodomethane to show the faster rate of S_N2 reaction with potassium cyanide? Explain your choice.

9 Show a reaction pathway, including structural formulas, for the two-step conversion of:

a 1-bromopropane to 1-butanamine

b 1-chlorobutane to pentanoic acid.

9.3 NUCLEOPHILIC SUBSTITUTION REACTIONS

The reactions of halogenoalkanes with ammonia and potassium cyanide to produce amines and nitriles are classic examples of nucleophilic substitution reactions by the S_N2 mechanism. Common nucleophiles, in addition to ammonia and the cyanide ion, include water and the hydroxide ion. Nucleophilic substitutions provide useful methods for preparing a number of compounds of different functional groups and chain lengths. To further understand this important class of reactions, let us consider the factors influencing the type and rate of nucleophilic substitution reactions of halogenoalkanes. Three factors to consider in any nucleophilic substitution reaction are the nature of the nucleophile, the substrate (the organic compound undergoing substitution) and the leaving group (the atom or group of atoms being displaced in the reaction).

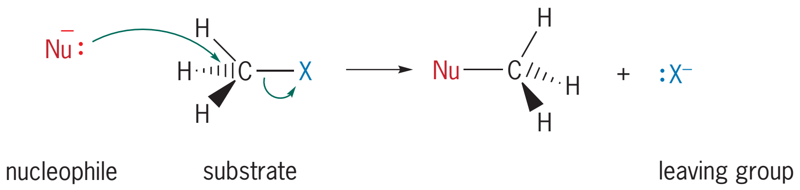


Figure 9.3.1 The substrate, nucleophile and leaving group all influence the rate of nucleophilic substitution reactions.

The nature of the nucleophile in S_N2 reactions

AS **20.2.1**
Explain why the hydroxide ion is a better nucleophile than water. © IBO 2007

The nature of the attacking nucleophile plays a major role in the S_N2 reaction. Any species, either neutral or negatively charged, can act as a nucleophile, provided that it has an unshared pair of electrons (and so can act as a Lewis base). A vast range of nucleophiles is used in reactions with halogenoalkanes, including ammonia and the cyanide ion considered on page 291–293, and the water molecule and hydroxide ion considered earlier in the synthesis of alcohols. How do these various nucleophiles compare in nucleophilicity? We can define nucleophilicity as the affinity of a species for the slightly positively charged carbon atom of the C–X bond. This nucleophilicity will vary with the substrate and solvent involved. To simplify comparisons, consider the relative reactivity of various nucleophiles when reacted with bromomethane in aqueous ethanol.

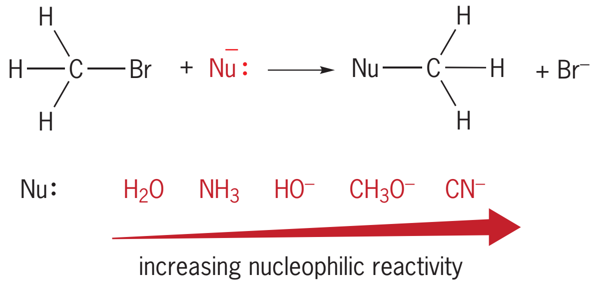


Figure 9.3.2 Relative rate of reaction of bromomethane with various nucleophiles in an S_N2 reaction.

For a species attacking an atom with a slight positive charge, we would expect that the more dense the charge on the attacking atom or group of atoms, the greater the reactivity, and hence the faster the rate of reaction.
When comparing nucleophiles with equivalent attacking atoms such as CH_3O^-, HO^- and H_2O, the negatively charged ions are stronger nucleophiles than water. The hydroxide ion, HO^-, is therefore a stronger nucleophile than the uncharged water molecule. Notice that the order of nucleophilicity here approximately parallels the order of base strength of the nucleophile; that is, the stronger the base (the lower its pK_b), the more reactive is the nucleophile.

TABLE 9.3.1 COMPARISON OF BASICITY AND NUCLEOPHILICITY

Nucleophile	H_2O	NH_3	HO^-	CH_3O^-
Relative rate of S_N2 reaction with CH_3Br	0.001	0.7	16	25
pK_b of the base	15.7	4.8	–1.7	–1.5

When comparing nucleophiles of the same charge, such as NH_3 and H_2O, the less electronegative attacking atom will be the stronger nucleophile. The non-bonding electron pair on this less electronegative atom will be more easily donated to the attacking atom, as it is held less tightly. NH_3 is therefore a stronger nucleophile (and a stronger base) than water. Similarly, when comparing OH^- and CN^-, the CN^- ion is the stronger nucleophile as it contains the less electronegative attacking atom.

The nature of the leaving group in S_N2 reactions

20.2.2 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on the identity of the halogen. © IBO 2007

In the S_N2 reaction of a halogenoalkane, the nature of the halogen leaving group—the halogen that is displaced by the attacking nucleophile—is also important in determining reaction rate. Two factors may be considered: the polarity and strength of the C–X bond.

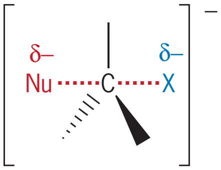
- The greater the polarity of the C–X bond, the greater the attraction for the attacking nucleophile. The C–F bond would therefore be expected to react more readily than the C–Cl bond, because of the greater bond polarity (in turn due to the greater electronegativity of the fluorine atom).
- The strength of the C–X bond decreases in the order C–F, C–Cl and C–I. If bond strength (or the ease of breaking of the C–X bond) was important, we would expect the C–I bond to react more readily than the C–F bond.

The order of reactivity of the various C–X halogenoalkanes is shown in table 9.3.2. Note that the C–I halogenoalkane reacts much more readily than the C–F halogenoalkane, so that it is the decreasing bond strength that is the key factor in increasing the rate of S_N2 reactions (and not the C–X bond polarity factor).

TABLE 9.3.2 COMPARISON OF LEAVING GROUP (X^-) WITH BOND STRENGTH (C–X)

Halogen	F	Cl	Br	I
C–X bond strength ($kJ\ mol^{-1}$)	484	338	276	238
Relative reactivity of X^- as a leaving group	1	200	10 000	30 000

What of other non-halogen leaving groups? The best leaving groups are found to be those that best stabilize a negative charge. To explain this, consider the transition state formed in the single step S_N2 reaction. In this transition state the negative charge is distributed over both the nucleophile (Nu) and the leaving group (X). The greater the stabilization of the negative charge, the lower is the energy of the transition state. Lowered energy of the transition state means a more rapid reaction. Halogens generally, and the larger bromine and iodine atoms in particular, stabilize negative charge effectively, making them good leaving groups. Poor leaving groups such as F^-, OH^- and NH_2^- are not easily displaced by nucleophiles. In fact fluoroalkanes, alcohols and amines do not normally undergo S_N2 reactions.



In the transition state in S_N2, the negative charge is distributed over both the nucleophile (Nu) and the leaving group (X).

Figure 9.3.3 Good leaving groups are able to stabilize the charge on the transition state in an S_N2 reaction.

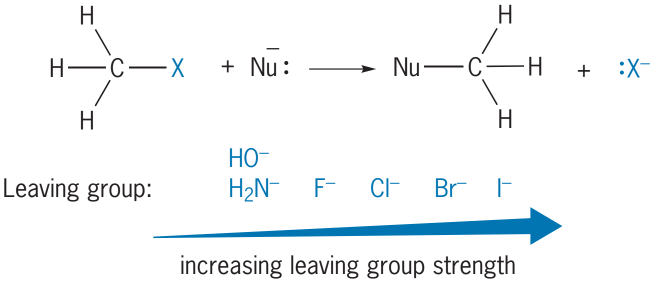


Figure 9.3.4 Relative rate of reaction of various leaving groups in an S_N2 reaction.

The nature of the substrate in S_N2 reactions

The formation of the transition state in the S_N2 reaction involves the nucleophile attacking and partially bonding to the carbon atom holding the leaving group. The easier it is for this attack to occur, the easier (and faster) the reaction will be. The idea of **steric hindrance** is an important consideration here. In the S_N2 reaction the nucleophile must approach close enough to the carbon atom being attacked for bonding to occur. If large, bulky alkyl groups crowd this approach, the reaction will be hindered. A change in reactivity due to the spatial arrangement of groups of atoms is known as steric hindrance. A bulky substrate, such as a tertiary halogenoalkane, will hinder the formation of the transition state and so slow the reaction. As seen in figure 9.3.5, the difficulty of attack by the nucleophile increases as the number of alkyl side groups increases. Thus attack of bromomethane by a nucleophile is much easier than the attack of bromoethane. Similarly, attack of a secondary halogenoalkane is hindered, and attack of a tertiary halogenoalkane is severely hindered. As the number of alkyl groups attached to the reactive carbon increases, the reactivity towards S_N2 substitution decreases. In energy terms, crowding by the alkyl groups raises the energy of the transition state and so slows the reaction.

AS 20.2.3
Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on whether the halogenoalkane is primary, secondary or tertiary.
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Due to these alkyl group steric hindrance effects, S_N2 reactions only occur readily at accessible sites. For this reason they are only useful as synthetic reactions for primary halogenoalkanes and a few of the simple secondary halogenoalkanes. We have considered the effects on S_N2 reaction rate of the nature of the nucleophile, the leaving group and the substrate. For halogenoalkanes, the more reactive the nucleophile, the weaker the C–X bond and the less hindrance the substrate offers to the nucleophile, the faster will be the S_N2 reaction. These effects may be summarized by considering energy diagrams for the S_N2 reaction (figure 9.3.6).

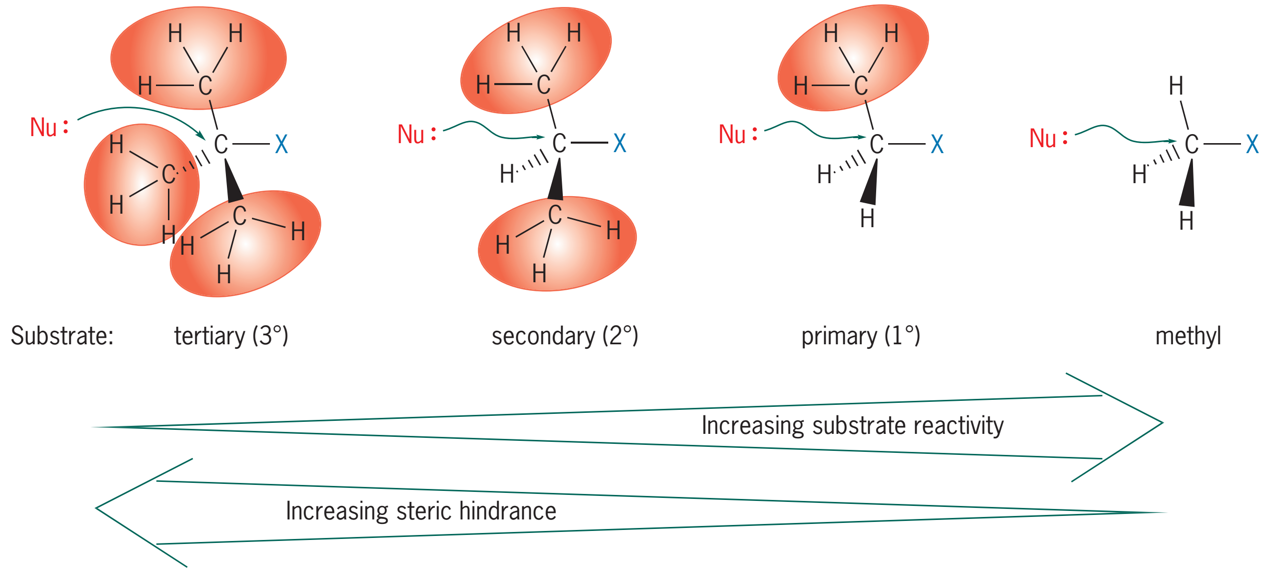


Figure 9.3.5 Relative rate of reaction of various substrates in an S_N2 reaction.

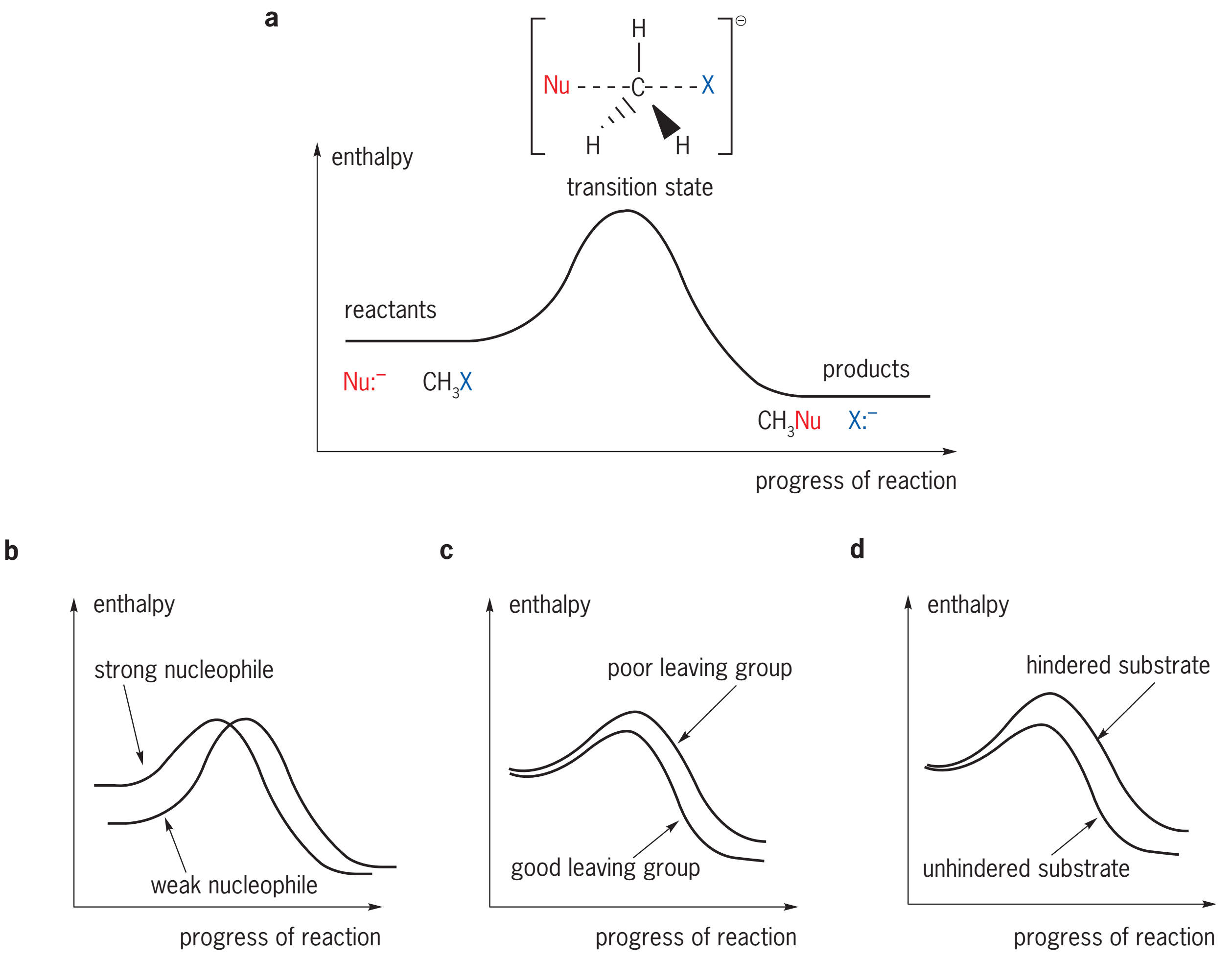


Figure 9.3.6 (a) Energy profile for the S_N2 reaction of a halogenoalkane with a nucleophile, Nu. Energy profiles showing the effects of the nature of (b) the nucleophile, (c) the leaving group and (d) the substrate.

Factors affecting reaction rate in S_N1 reactions

Given the summary in figure 9.3.6, what would you predict about the relative rates of the two nucleophilic substitutions shown in figure 9.3.7?

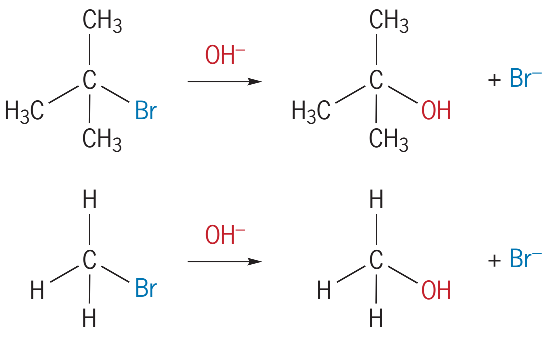


Figure 9.3.7 Which of the two nucleophilic substitutions shown would you predict to be the faster?

The tertiary substrate (2-bromo-2-methylpropane) offers considerable steric hindrance to the nucleophile, OH^-. Both reactions involve the same leaving group, bromine. Reaction for 2-bromo-2-methylpropane would be predicted to be slow. Reaction, however, is found to be quite rapid, and many, many times faster than the corresponding reaction between bromomethane and hydroxide ion! Why?

A study of the reaction kinetics reveals that the reaction rate for the 2-bromo-2-methylpropane reaction depends only on the halogenoalkane concentration, and is independent of the hydroxide ion concentration.

Reaction rate = k[RX]

This was not the case for the S_N2 reactions considered earlier, so clearly this nucleophilic reaction occurs by a different mechanism—unimolecular nucleophilic substitution, S_N1. The S_N1 mechanism is shown in figure 9.3.8.

This two-step process involves the formation of the intermediate **carbocation** by the slow, rate-limiting **heterolytic fission** of the halogenoalkane. The carbocation then rapidly reacts with the nucleophile.

The nature of the nucleophile played a significant role in the rate of the S_N2 reaction. However, in the S_N1 reaction the nucleophile is not involved in step 1, the slow rate-limiting carbocation formation step. The nucleophile does not enter the reaction until step 2, after carbocation formation. Thus in S_N1 reactions the nature of the nucleophile is not important in determining the rate of the reaction.

In contrast to the nucleophile, the leaving group is directly involved in the S_N1 rate-limiting first step. As was the case for S_N2 reactions, the strength of the C–X bond is the important factor. Thus, the weaker C–I bond results in a faster reaction than for the stronger C–Cl bond.

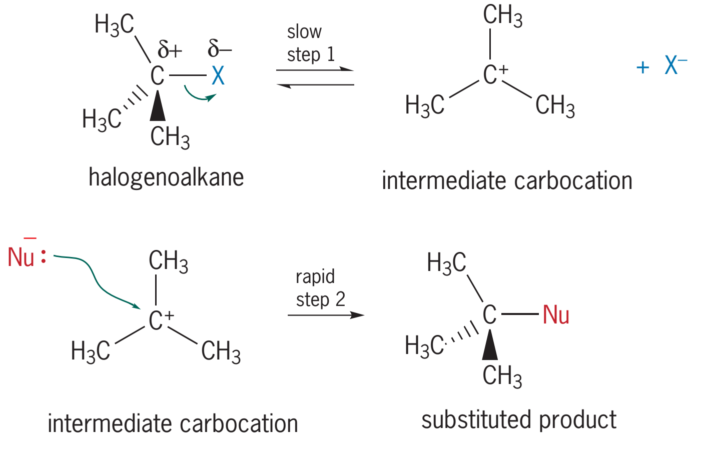


Figure 9.3.8 Nucleophilic substitution by the S_N1 mechanism.

The ease and rate of the S_N1 reaction depends directly on the ease of formation and the stability of the carbocation. The idea of stabilizing the charge on the carbocation is an important consideration here. As we have seen, the C–X bond in a halogenoalkane is polarized, with the carbon atom carrying a slight positive charge. If the C–X carbon atom is bonded to another carbon atom, this polarization or induced charge can be transmitted further. Thus the C–C bond becomes slightly polarized, as shown in figure 9.3.9. If another carbon atom is bonded to the C–X carbon atom, further inductive effect occurs. This tendency of alkyl groups to 'push' the bonding electron pair towards the carbon of the C–X bond is known as the **positive inductive effect**.

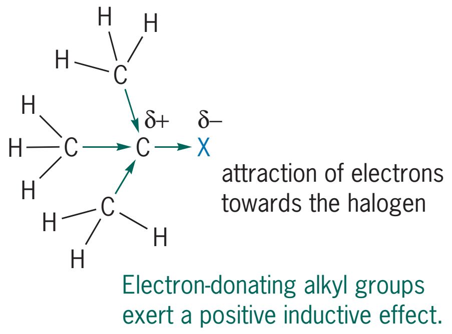


Figure 9.3.9 Alkyl groups exert a positive inductive effect, stabilizing a carbocation.

WORKSHEET 9.2
Nucleophilic substitution reactions

Positive inductive effects of alkyl groups in a carbocation stabilize the ion. The effect of the electron 'pushing' alkyl groups is to allow the positive charge of the central carbon in the carbocation to be dispersed, and so to be more stabilized. This stabilization of the positive charge increases the likelihood of formation of the carbocation. The order of stability of carbocations is therefore related to the number of alkyl groups attached to the C–X carbon atom. The three alkyl groups in a tertiary carbocation exert a greater positive inductive effect than the two groups in a secondary carbocation. These two groups in turn exert a greater effect than the one group in a primary carbocation. For S_N1 reactions the order of reactivity parallels the order of carbocation stability.

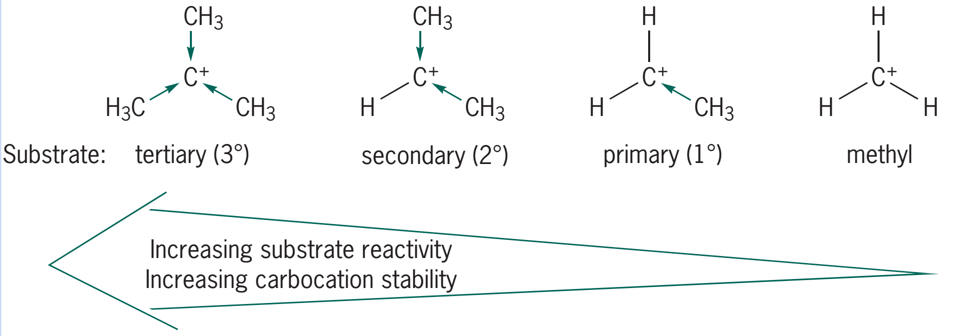


Figure 9.3.10 The relative reactivity of various substrates in an S_N1 reaction parallels the order of stability of the carbocation.

Note that this is the reverse of the reactivity order for S_N2, for which the main influence of the alkyl groups was one of steric hindrance. Reaction by the S_N2 mechanism was therefore favoured for primary halogenoalkanes, and non-existent for tertiary halogenoalkanes. Reaction by the S_N1 mechanismis favoured for tertiary halogenoalkanes, and non-existent for primary halogenoalkanes. Table 9.3.3 summarizes the effects of nucleophiles, leaving groups and substrates for both S_N1 and S_N2 reactions of halogenoalkanes.

TABLE 9.3.3 FACTORS AFFECTING S_N1 AND S_N2 REACTIONS OF HALOGENOALKANES

Factor	Effect on S_N2 reaction rate	Effect on S_N1 reaction rate
Nucleophile	Charged species are stronger nucleophiles than neutral species, e.g. **OH^- is a stronger nucleophile than H_2O**. Stronger bases are stronger nucleophiles, e.g. NH_3 is a stronger nucleophile than H_2O.	No effect. The nucleophile does not influence step 1, the rate-determining heterolytic fission step.
Halogen leaving group	The weaker the C–X bond the stronger the leaving group, e.g. the weaker C–I bond means that CH_3I is more reactive than CH_3Cl, which contains the stronger C–Cl bond.	As for S_N2. The C–X bond strength influences the ease of step 1, the rate-determining heterolytic fission step.
	The order of reactivity for halogenoalkanes is C–I > C–Br > C–Cl.	
Substrate	Steric hindrance by alkyl groups attached to the C–X carbon atom influence ease of reaction. **Primary halogenoalkanes show the least steric hindrance and so react faster than tertiary halogenoalkanes.**	Positive inductive effects by alkyl groups attached to the C–X carbon stabilize the carbocation and so influence ease of reaction. **Tertiary halogenoalkanes show the greatest inductive or stabilizing effect and so react faster than primary halogenoalkanes.**

Section 9.3 Exercises

1 2-Bromo-2-methylpropane reacts with aqueous sodium cyanide by an S_N1 mechanism.

- **a** Use diagrams to illustrate what is meant by an S_N1 mechanism for this reaction.
- **b** Why is it referred to as S_N1?

2 Iodomethane reacts with aqueous sodium cyanide by an S_N2 mechanism.

- **a** Use diagrams to illustrate what is meant by an S_N2 mechanism for this reaction.
- **b** Why is it referred to as S_N2?

3 The equation for a nucleophilic substitution reaction is given below.

$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

The reaction takes place by means of a two-step mechanism.

- **a** For this reaction, name the:
  - **i** nucleophile
  - **ii** leaving group
  - **iii** type of halogenoalkane substrate (primary, secondary or tertiary)
  - **iv** type of substitution (S_N1 or S_N2).
- **b** Using structural diagrams, draw equations for each step of the reaction.

4 The equation for a nucleophilic substitution reaction is given below.

$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$

The reaction takes place by means of a one-step mechanism.

a For this reaction, name the:

- **i** nucleophile
- **ii** leaving group
- **iii** type of halogenoalkane substrate (primary, secondary or tertiary)
- **iv** type of substitution (S_N1 or S_N2).

b Using structural diagrams, draw the mechanism for the reaction.

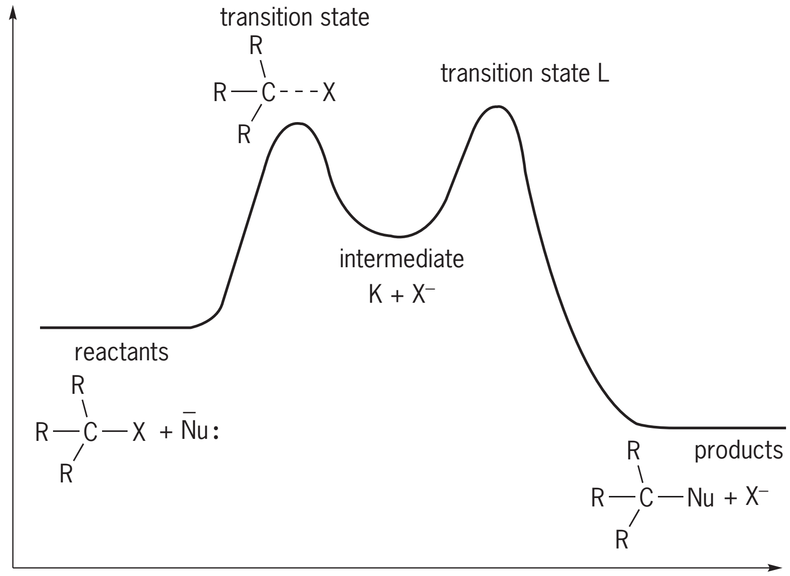
5 Identify which of the following reactions would involve the formation of a positive ion intermediate. Explain your choice.

- **I** $CH_3CH_2CH_2Br + OH^-$
- **II** $(CH_3)_3CBr + OH^-$

6 Identify which reagent in each of the following pairs is the stronger nucleophile. Explain your choices.

a H_2O or OH^-

b H_2O or H_2S



7 The graph (above) shows the energy profile for a nucleophilic substitution reaction.

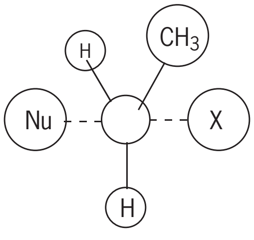
a Identify the reaction as S_N1 or S_N2.

b Draw a structural diagram of the intermediate species labelled as K on the diagram.

c State the name given to this type of intermediate.

d Draw a structural diagram of the transition state labelled as L on the diagram.

8 The diagrams below show the transition states formed in a number of nucleophilic substitution reactions.



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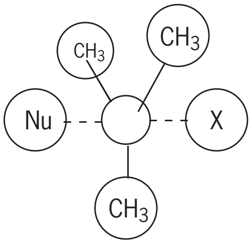

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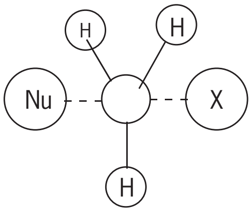

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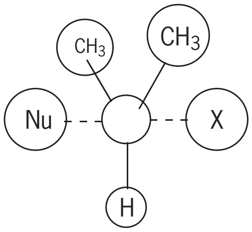


IV

a Identify these reactions as S_N1 or S_N2.

b Which transition state would be the most stable and hence lead to the fastest reaction rate? Explain your choice.

9 State and explain which of the following compounds you would expect to react more rapidly by an S_N2 mechanism.

$(CH_3)_3CCH_2Br$ or $CH_3CH_2CH_2CH_2CH_2Br$

10 **a** Deduce the order of reactivity of the following compounds towards S_N2 reaction:

CH_3Br, $(CH_3)_3CBr$, $(CH_3)_2CHBr$

b Deduce the order of reactivity of the following compounds towards S_N1 reaction:

CH_3CH_2Br, $(CH_3)_3CBr$, $(CH_3)_2CHBr$

11 Consider the reaction between a halogenoalkane, RX, and sodium hydroxide in a solvent of water and ethanol. Copy and complete the following table comparing the S_N1 and S_N2 mechanisms for this reaction with respect to each of the characteristics listed in the table.

Characteristic	**S_N2 reaction**	**S_N1 reaction**
Kinetic order (*first or second?*)		
Relative rate of reaction for RCl, RBr and RI		
Effect on reaction rate of doubling the concentration of RX		
Effect on reaction rate of doubling the concentration of OH^-		

12 Arrange these reactions in order of decreasing reaction rate. Explain your order.

I $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$

II $(CH_3)_3CI + OH^- \rightarrow (CH_3)_3COH + I^-$

III $(CH_3)_3CI + H_2O \rightarrow (CH_3)_3COH + HI$

9.4 ELIMINATION REACTIONS

AS 20.3.1 **Describe, using equations, the elimination of HBr from bromoalkanes. © IBO 2007**

We have looked closely at the nucleophilic substitution reactions of halogenoalkanes. This has provided an illustration of the effects of the structure of the reactants on the rate of reaction. We may predict then the type of mechanism (S_N1 or S_N2) that would be expected for a particular combination of reactants.

Consider the reaction of bromoethane with a warm, dilute aqueous sodium hydroxide solution. We would expect an S_N2 reaction to occur, as the substrate is a primary halogenoalkane, containing a good leaving group, reacting with a strong nucleophile. The OH^- acts as a nucleophile, Br^- is the displaced leaving group, and ethanol forms. However, if the reaction is repeated using a hot solution of sodium hydroxide in ethanol and the mixture is refluxed, the product obtained is ethene, not ethanol!

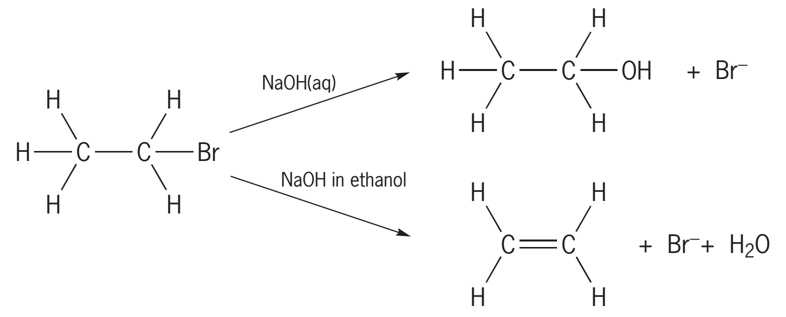


Figure 9.4.1 The same reactants produce different products when the reaction conditions are altered.

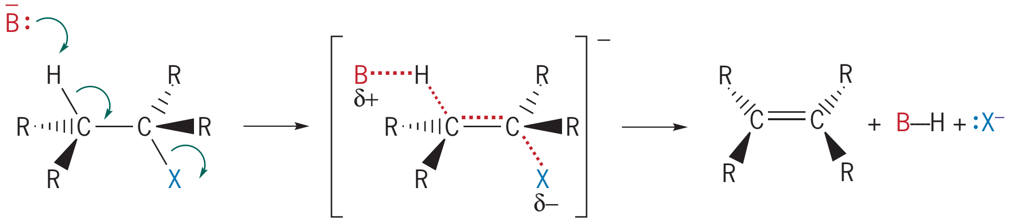
This reaction provides an example of how the same reactants can produce completely different products under different conditions. Production of ethene here is clearly not a substitution reaction. Another reaction mechanism occurs, resulting in the elimination of HBr from the halogenoalkane. This **elimination reaction** is the reverse of an addition reaction. In elimination, a double bond forms between adjacent carbon atoms as products form from the atoms removed from the adjacent carbon atoms.

These elimination reactions from halogenoalkanes are a useful method for preparing alkenes. However, as halogenoalkanes undergo both substitution and elimination reactions when reacted with basic reagents such as OH^-, there will always be competition between the two reactions. An understanding of the factors that influence both reaction types is therefore necessary if the correct conditions are to be chosen for the successful synthesis of a desired product.

AS 20.3.2 **Describe and explain the mechanism for the elimination of HBr from bromoalkanes. © IBO 2007**

Just as there are two mechanisms for substitution reactions, there are two mechanisms for elimination reactions. The **E2** reaction (**bimolecular elimination**) occurs when the halogenoalkane reacts with a strong base such as hydroxide ion (OH^-) or alkoxide ion (RO^-). In common with the S_N2 reaction, the E2 reaction involves a single step. The attacking base begins to remove a hydrogen atom from the carbon atom adjacent to the carbon atom holding the leaving group (X). At the same time the C–H bond begins to break, a double bond begins to form between the carbon atoms, and the leaving group begins to depart. The leaving group will take the C–X bond electron pair with it. The rate of reaction depends on the concentration of both the attacking base and the halogenoalkane (hence the 'bimolecular' label).

$$\text{Rate} = k[\text{RX}][\text{Base}]$$



Base B attacks a neighbouring hydrogen atom.

A transition state forms with partial B······H, H······C, C═C and C······X bonds.

An alkene forms. A conjugate acid forms. Leaving group is displaced.

Figure 9.4.2 The mechanism of the E2 reaction of a halogenoalkane with a base.

The actual base involved in the hydroxide ion and halogenoalkane reaction may be the ethoxide ion, $CH_3CH_2O^-$, rather than OH^-. Reaction occurs in an ethanol solution at high concentration and high temperature. Ethanol may react with the hydroxide ion to produce the ethoxide ion, $CH_3CH_2O^-$. This ion is a stronger base than OH^-, and so favours the elimination reaction. In general, stronger bases favour elimination reactions and make them proceed faster. In addition, high temperatures favour elimination over substitution.

The **E1** reaction (**unimolecular elimination**) is somewhat like the S_N1 reaction in that the first step involves the formation of the carbocation by the heterolytic fission of the C–X bond. Reaction rate is independent of the concentration of the base, and depends only on the concentration of the halogenoalkane.

$$\text{Rate} = k[\text{RX}]$$

Following formation of the carbocation, removal of a proton from the cation by the base occurs to yield the alkene (rather than substitution by the nucleophile as occurs in S_N1). E1 and S_N1 reactions occur in competition with each other due to their common carbocation formation step. The best substrates for E1 reactions are therefore the same as those for S_N1; that is, tertiary halogenoalkanes in which the carbocation is stabilized by the positive inductive effect of the alkyl groups. Basic nucleophiles favour the E1 reaction over the S_N1 reaction.

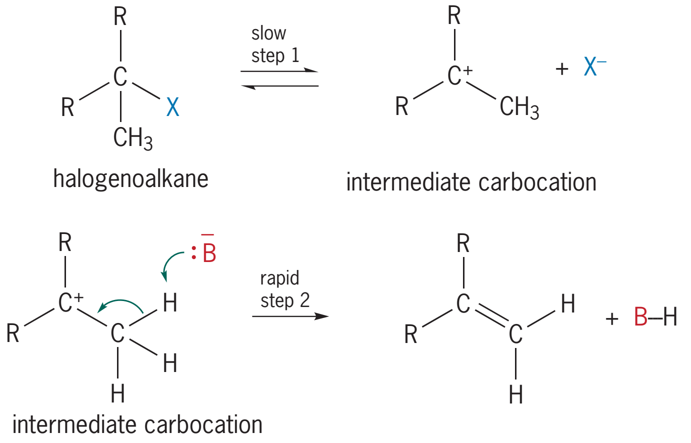


Figure 9.4.3 The mechanism of the E1 reaction of a halogenoalkane with a base.

We have now seen four possible reaction mechanisms for the reaction of a halogenoalkane with a nucleophile. How then can we predict what will happen when a given halogenoalkane reacts with a given nucleophile? Will the mechanism be S_N1, S_N2, E1 or E2? While it is not possible to be sure, some generalizations can be made (see table 9.4.1).

It should also be noted that the nature of the solvent used plays a role. For example, using hot ethanol as the solvent favours E2 over S_N2 for reaction of OH^- with CH_3CH_2Br, resulting in the formation of ethene, rather than ethanol.

TABLE 9.4.1 A SUMMARY OF SUBSTITUTION AND ELIMINATION REACTIONS

Halogenoalkane	S_N1	S_N2	E1	E2
Primary RCH_2X	Does not occur	Most favoured	Does not occur	Can occur when strong bases, e.g. RO^-, are used
Secondary R_2CHX	Can occur	Occurs in competition with E2	Can occur	Favoured when strong bases, e.g. RO^-, are used
Tertiary R_3CX	Occurs in competition with E1	Does not occur	Occurs in competition with S_N1	Favoured when strong bases, e.g. RO^-, are used

Section 9.4 Exercises

1 The equation for an elimination reaction is given below.

$(CH_3)_2CHBr + OH^- \rightarrow CH_3CHCH_2 + H_2O + Br^-$

The reaction takes place by means of a one-step mechanism.

a For this reaction, state the name of the:
  - **i** attacking base
  - **ii** leaving group
  - **iii** type of halogenoalkane substrate (primary, secondary or tertiary).

b Using structural diagrams, draw the mechanism of the reaction.

2 The equation for an elimination reaction is given below.

$(CH_3)_3CBr + CH_3CH_2O^- \rightarrow (CH_3)_2CCH_2 + CH_3CH_2OH + Br^-$

The reaction takes place by means of a two-step mechanism.

a For this reaction, state the name of the:
  - **i** attacking base
  - **ii** leaving group
  - **iii** type of halogenoalkane substrate (primary, secondary or tertiary).

b Using structural diagrams, draw the mechanism of the reaction.

3 **a** Explain why primary halogenoalkanes do not undergo an elimination reaction by an E1 mechanism.

b Explain why tertiary halogenoalkanes do not undergo substitution reaction by an S_N2 mechanism.

4 Explain how an elimination reaction may be thought of as the reverse of an addition reaction.

5 State whether the following reactions would be expected to be S_N1, S_N2, E1 or E2.

a 1-chlorobutane + NaCN → pentanenitrile

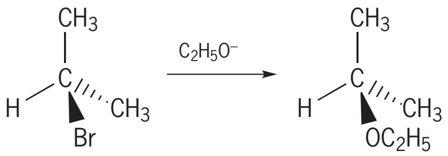
b 1-bromobutane + CH_3CH_2COK →1-butene

c 2-chloro-2-methylpropane + H_2O → 2-methylpropan-2-ol

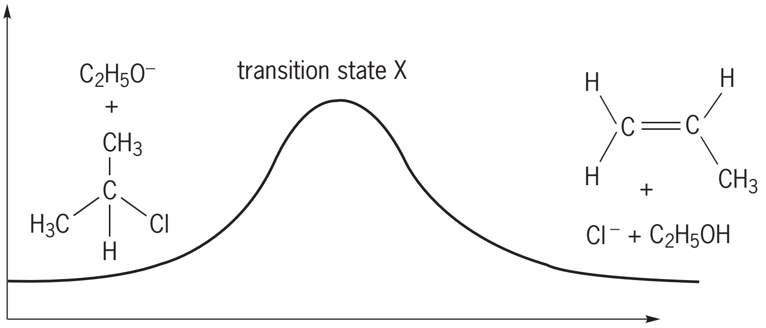
d 3-chloropentane + KOH → 2-pentene

6 The reaction shown was attempted.

A product was obtained, but it was not the one shown in the equation. Suggest the likely identity of the product, and explain how it formed.



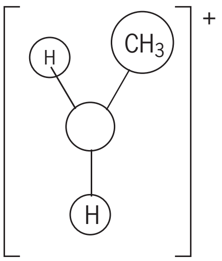
7 The graph below shows the energy profile for an elimination reaction.



a Identify the reaction as E1 or E2.

b Draw a structural diagram of the transition state labelled as X on the diagram.

8 The diagrams below show the intermediates formed in a number of elimination reactions.



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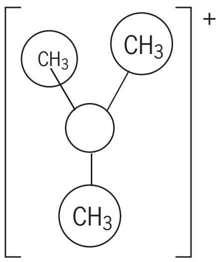

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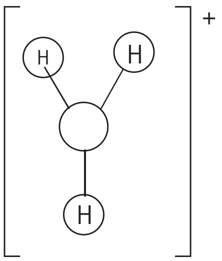

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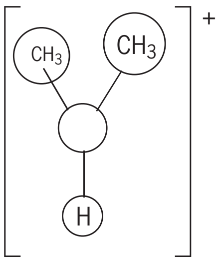


IV

a Identify these reactions as E1 or E2.

b Which intermediate would be the most stable and hence lead to the fastest reaction rate? Explain your choice.

9.5 REACTIONS INVOLVING ESTERS AND AMIDES

Esters

AS 20.4.1 Describe, using equations, the reactions of alcohols with carboxylic acids to form esters, and state the uses of esters. © IBO 2007

Carboxylic acids react with alcohols to form esters (RCOOR′). An ester is derived from the acid by the replacement of the –OH in the carboxyl group with an –OR group from the alcohol. Thus ethanoic acid, CH_3COOH, reacts with methanol, CH_3OH, to produce methyl ethanoate, CH_3COOCH_3. Water is also produced in the reaction. This type of reaction, in which two molecules containing functional groups react to produce a larger molecule and a small molecule (often water) is eliminated, is called a **condensation reaction**. Condensation reactions are an important class of reaction. They feature in the formation of synthetic polymers such as polyester and nylon, and in the formation of natural polymers including proteins, carbohydrates, lipids and nucleic acids.

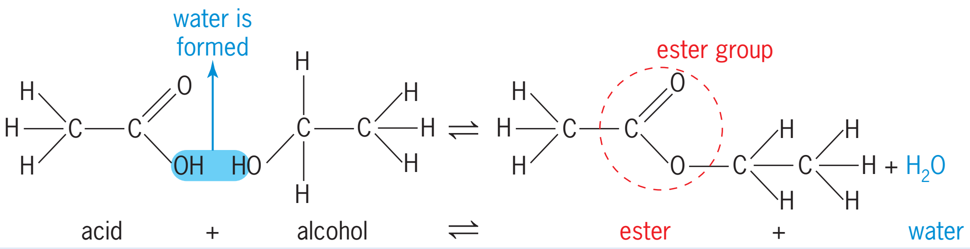


Figure 9.5.1 Esters form by the condensation reaction of an acid and an alcohol.

PRAC 9.1
Preparation of esters

The condensation reaction of an acid and an alcohol to produce an ester is an acid-catalysed reversible equilibrium process. The acid catalyst shifts the equilibrium to the right by removing water. In the laboratory, the formation of an ester is easily shown. Small quantities of ethanol, glacial ethanoic acid and concentrated sulfuric acid (the catalyst) are mixed in a test tube. The mixture is then warmed gently for a few minutes, after which it is poured into cold water. The fruity smell of ethyl ethanoate (ethyl acetate) will now be detected. Recall that esters often have a characteristic sweet fruity odour, in contrast to the often pungent odour of carboxylic acids.

Esters are named from the acid and alcohol from which they are prepared (see page 286). Thus given the name of an ester, its reactant acid and alcohol are readily determined. For example, methyl propanoate is produced by reaction of meth*anol* and propan*oic acid*.

Esters undergo acid and alkaline hydrolysis to yield carboxylic acids and alcohols. They react with ammonia to produce amides.

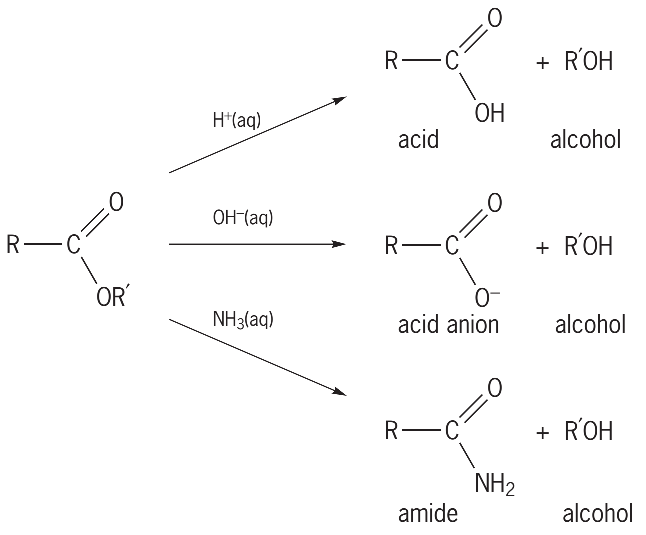


Figure 9.5.2 Reactions of esters.

CHEM COMPLEMENT

Pain-relieving esters

An important ester is the one commonly known as acetylsalicylic acid, or aspirin, used in huge quantities as an analgesic (pain killer). Aspirin is the most widely known and used of all drugs. Used to relieve headaches and other pains, it also reduces fevers, helps prevent heart attacks and strokes, and shows promise in helping fight pancreatic, colonic and prostate cancers. The concentration of aspirin in the small tablet is low, yet two tablets can have a significant effect within 20 minutes.

Aspirin can be derived from the bark of willow trees. Herbal medicines to treat aches and pains have made effective use of the bark since Roman times. The bark contains salicin, which is converted within the body to salicylic acid, and it is this substance that is the active ingredient in preparations designed to alleviate the symptoms of headaches, inflammation and fever. But salicylic acid severely irritates the lining of the stomach, and so an alternative was sought by the chemists of the 19th century. In 1898, Felix Hoffman, a chemist working in Germany for the Bayer Company, developed a feasible process for manufacturing an ester form of salicylic acid called acetylsalicylic acid, which was patented under the trade name 'Aspirin'.

Aspirin can be produced in the school laboratory by reacting salicylic acid with glacial ethanoic acid in the presence of a concentrated sulfuric acid catalyst.

An alternative condensation reaction produces oil of wintergreen, the active ingredient in heat rubs. While the laboratory synthesis of these esters is relatively straightforward, the industrial production is somewhat more complex!

In industry, a 7500 dm^3 tank fitted with a water-cooled reflux condenser and numerous automatic temperature sensors is used as the major reaction vessel. Into the vessel is placed 1530 kg of acetic anhydride, $(CH_3CO)_2O$, dissolved in 1200 kg of the solvent toluene. 1380 kg of salicylic acid is then added and the mixture is heated to between 88°C and 92°C. This temperature is maintained for 20 hours, after which the solution is transferred to aluminium cooling tanks and allowed to cool for 3 to 4 days. Once the liquid has cooled to room temperature, much of the acetylsalicylic acid will have precipitated out as large crystals. The liquid is removed by filtration or centrifuging, and has the following composition: 180–270 kg of unprecipitated acetylsalicylic acid, 510 kg of acetic anhydride, 600 kg of acetic acid and 1200 kg of toluene. Is it feasible to simply throw away in excess of 2.5 tonnes of material in order to produce just 1.5 tonnes of the desired material? Obviously not! A number of further treatment processes are undertaken to reclaim the toluene solvent for future use, remove the acetic acid for subsequent sale as a valuable by-product, and further react the unused acetic anhydride with more salicylic acid. Eventually, between 1780 kg and 1795 kg of pure acetylsalicylic acid can be produced using these quantities.

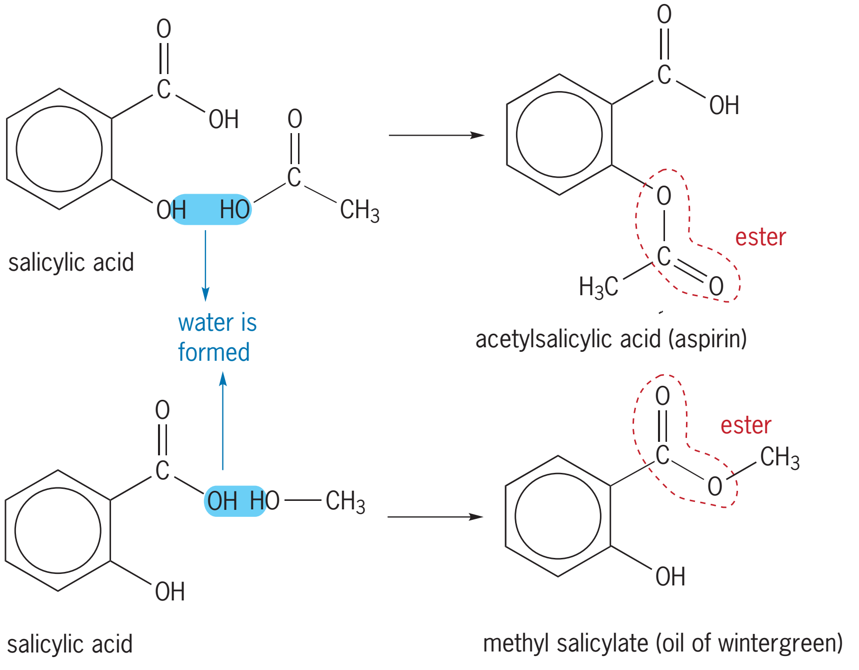


Figure 9.5.3 Synthesis of aspirin and oil of wintergreen involves condensation reactions.

AS 20.4.2 Describe, using equations, the reactions of amines with carboxylic acids. © IBO 2007

Amides

Somewhat analogous to the production of esters from acids and alcohols is the condensation reaction to produce amides, $RCONH_2$. An amide is derived from the acid by the replacement of the –OH ion in the carboxyl group with an $–NH_2$ group from an amine or ammonia molecule.

Amides can be prepared by reaction of a carboxylic acid with either ammonia or an amine; for example, the reaction of ethanoic acid with ammonia to produce ethanamide and water. As for esters, the name of an amide is derived from the reactants used to prepare it. For simple amides produced by reaction of a carboxylic acid and ammonia, the name is simply that of the parent acid with the ending changed to -amide (see page 287). For example, methanamide is prepared from methan*oic acid* and ammonia. For substituted amides, the name again shows the reactant molecules used to prepare it. For example, *N*-methylpropanamide is prepared using methyl*amine* and propan*oic acid*. Similarly, *N*,*N*-dimethylethanamide is produced from *N*,*N*-dimethyl*amine* and ethan*oic acid*.

Interactive Animation: Formation of amide link

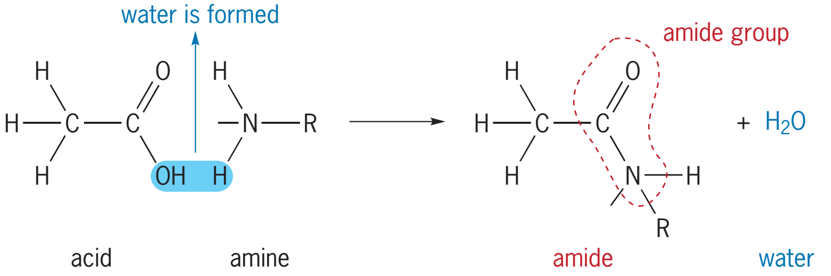


Figure 9.5.4 Amides can form by the condensation reaction of an acid and ammonia or an amine.

Although this reaction of a carboxylic acid and an amine can produce an amide, amides are difficult to prepare by this direct method. Since amines are basic they tend to convert the acid into its anionic form ($RCOO^-$). The ammonia nucleophile is now less likely to attack the carbon of the carboxyl group. Amides are therefore usually prepared by the reaction of an acyl chloride (RCOCl) with ammonia or an amine.

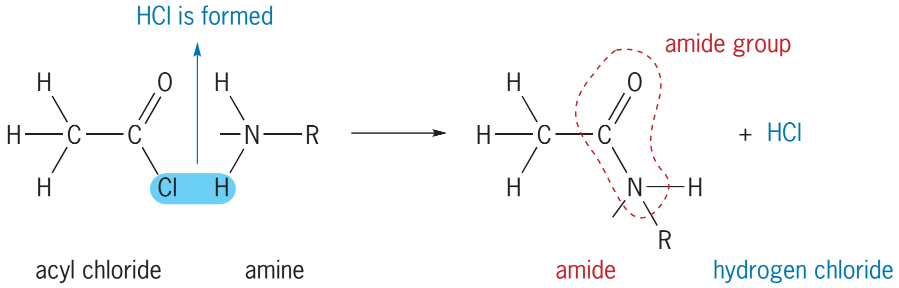


Figure 9.5.5 Amides are usually prepared by the condensation reaction of an acyl chloride and ammonia or an amine.

Amides are less reactive than esters, but will undergo acid or alkaline hydrolysis on heating to yield carboxylic acids and ammonia or amines. In fact, amides are sufficiently unreactive that the amide linkage is stable enough to form the basic unit from which proteins and nylon are made.

Polyesters and polyamides

Amino acids are molecules that contain both an amino and a carboxyl functional group. When both groups are attached to the same central carbon atom, a 2-amino acid results (also known as an α-amino acid). Twenty such 2-amino acids are found naturally, differing in the side group, R (see figure 9.5.6). These twenty 2-amino acids are the basic units of the proteins found in all living things.

Two amino acids can react together in a condensation reaction. Reaction of the amino group of one amino acid with the carboxyl group of the other produces a dipeptide, containing an amide group. A water molecule is formed, as shown in figure 9.5.7a. The amide linkage is also known here as a peptide bond. Note that each amino acid has two functional groups, so two different dipeptide products are possible. Can you draw the other possible dipeptide product when the two amino acids shown are reacted?

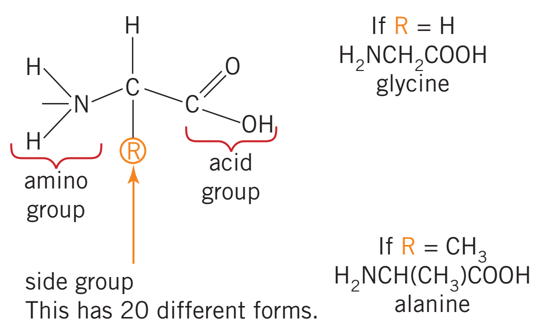


Figure 9.5.6 2-amino acids contain an amino and a carboxyl group attached to the same carbon atom.

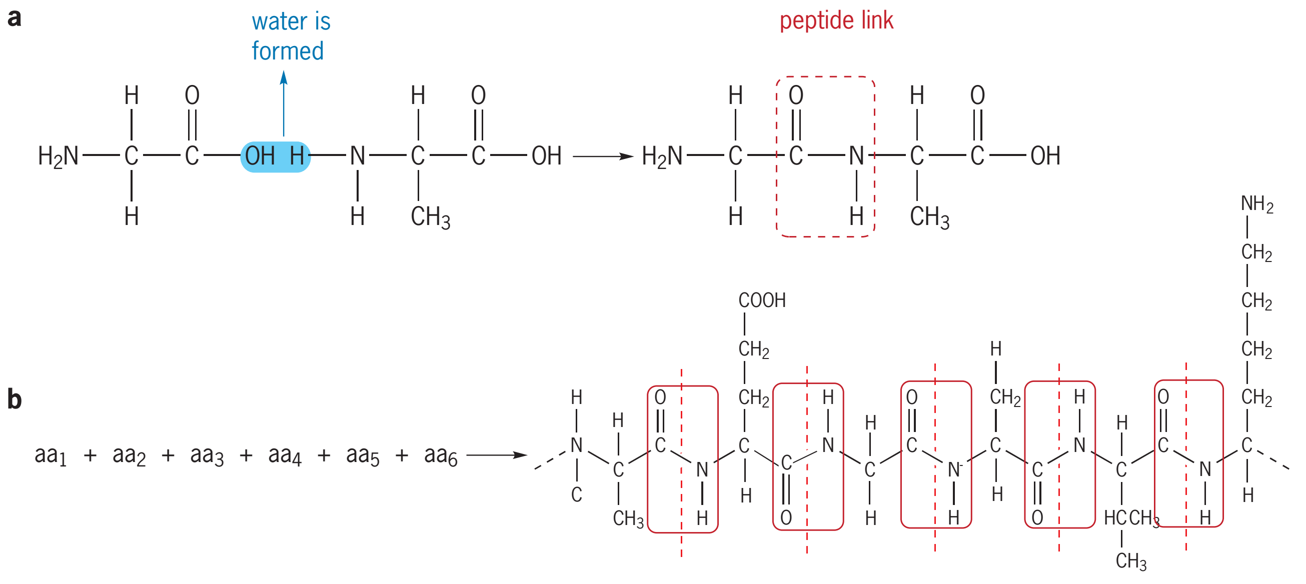
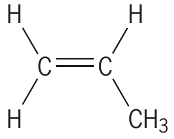
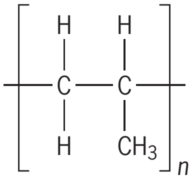
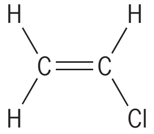
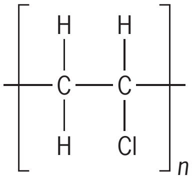
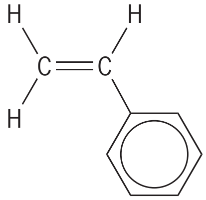
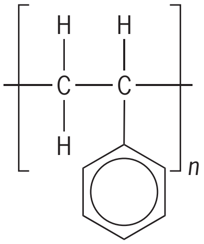
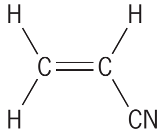
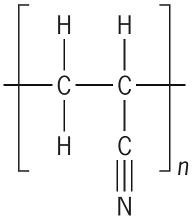


Figure 9.5.7 (a) Two amino acids undergo a condensation reaction to produce a dipeptide. (b) Condensation reactions between large numbers of amino acids produce long-chain protein molecules.

A look at the dipeptide reveals that, like the original acids, it contains two functional groups and so could react again in another condensation reaction. Continued reaction of the product can lead to production of a very large molecule composed of many amino acid units. The product is called a polypeptide or a protein.

Proteins are complex polymers. Recall from the Standard Level course that polymers are long chain molecules derived from small molecules known as monomers. Recall also that addition polymerization of monomers containing a double carbon–carbon bond produces a vast range of important polymers, including polyethene, polystyrene and polychloroethene (PVC).

TABLE 9.5.1 SOME ADDITION POLYMERS AND THEIR USES

Monomer	Polymer	Some Uses
Propene 	Polypropene 	Dishwasher-safe plastics, ice-cream containers 
Chloroethene (vinyl chloride) 	Polyvinyl chloride (PVC) 	Plastic wrap, plumbing, garden hoses 
Styrene 	Polystyrene 	Styrofoam insulation, cups, packing materials 
Propenenitrile 	Polypropenenitrile (acrylic) 	Acrylic fibres 

AS 20.4.4
Deduce the structures of the polymers formed in the reactions of amines with carboxylic acids. © IBO 2007

The **condensation polymerization reaction** of monomers containing two functional groups also produces a vast range of important polymers, including polyester, nylon and the naturally occurring proteins described above. Proteins might be termed naturally occurring polyamides. Synthetic polyamides include nylon. There is actually a range of nylons, but one of the most common is nylon 6.6. This is formed by the polymerization of 1,6-diamino hexane and hexanedioic acid.

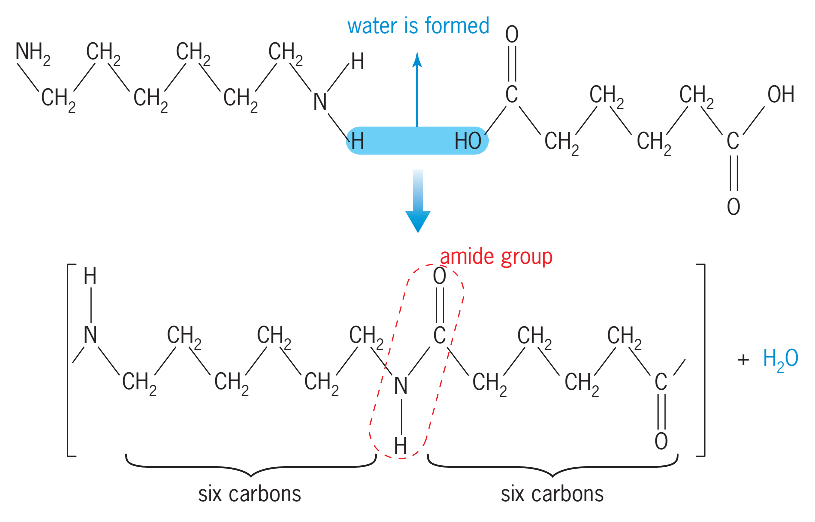


Figure 9.5.8 Nylon, a polyamide, is formed by condensation polymerization.

PRAC 9.2
Making nylon

Synthesis of nylon 6–10

The polyamide chains in nylon are cross-linked together by hydrogen bonding. These hydrogen bonds give nylon great tensile strength. The majority of nylon is used to make clothing, as well as carpets, rope and parachutes. It is also used in paint brushes, electrical parts and valves. The hardness and strength of nylon also lead to its use in machine gears and bearings.

20.4.3
Deduce the structures of polymers formed in the reactions of alcohols with carboxylic acids. © IBO 2007

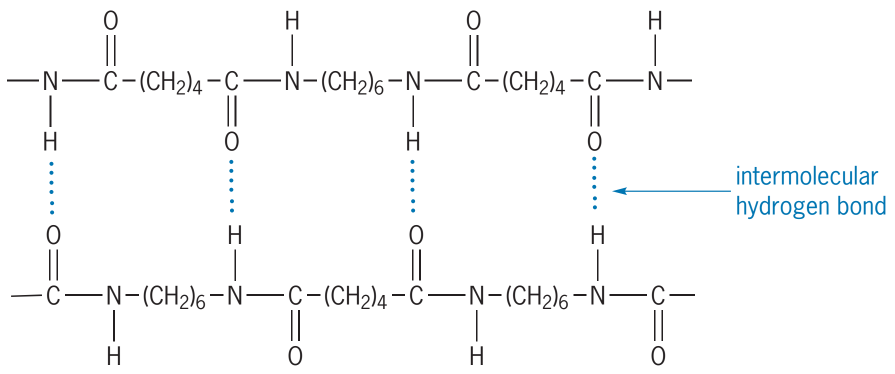


Figure 9.5.9 Intermolecular bonding gives nylon great tensile strength.

Another example of a synthetic condensation polymer is polyester. Again there is a range of polyesters, but a well-known example is the textile polyethene terephthalate (known as Terylene in the UK and Dacron in the USA). It is produced by the reaction of ethane-1,2-diol and benzene-1,4-dicarboxylic acid.

Figure 9.5.11 Polyester is used to make sails and parachutes.

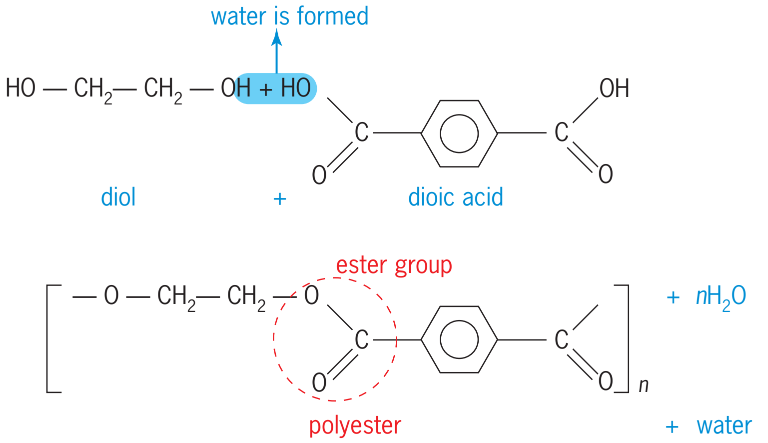


Figure 9.5.10 Polyester is formed by condensation polymerization.

Strong dipole–dipole attractions between the carbonyl groups on adjacent polyester molecules confer on polyester a high tensile strength. Polyester is widely used in clothing of all kinds as well as in cords, carpets and as patches to repair human arteries. It is used for yacht sails and parachutes because it is tough and does not readily decompose.

From the examples of nylon and polyester considered above, you will notice that a condensation polymer has a repeating unit that includes an amide or ester bond that is formed during polymerization. The polymer may be represented by drawing the repeating unit within a bracket, and using the subscript n to show the repetition occurring many times over (figure 9.5.10).

AS 20.4.5
Outline the economic importance of condensation reactions. © IBO 2007

WORKSHEET 9.3
Esters, amides, polyesters and polyamides

We have considered three condensation polymers—proteins, synthetic polyamides and polyesters. Many other condensation polymers exist, including polycarbonates (tough, clear polymers strong enough to be used as bulletproof windows), polyurethanes with a similar structure to nylon (used as foam rubber) and epoxyresins (powerful adhesives). Synthetic polymers, both addition and condensation, today find application in almost every industry and area of life, and there is little doubt that they will continue to be widely used in the future. We already have polymers that are stronger but much lighter than steel, polymers that conduct electricity, polymers used in replacement body parts, and polymers used extensively in the construction of cars and aircraft. Polymer use and polymer research is, and will continue to be, of significant economic importance. However, there is reason to pause for thought. Most synthetic polymers are ultimately derived from petroleum or natural gas. As supplies of these non-renewable resources dwindle, as we see them continually extracted and burnt as fuels, where does the long-term future of polymers lie? Is there anything to replace petroleum as the raw material for making polymers?

Section 9.5 Exercises

1 **a** State the name of the reagent and the conditions required to convert ethanoic acid to methyl ethanoate.

  b Write an equation for the reaction, using structural formulas.

  c Outline one physical and one chemical property that differs for ethanoic acid and methyl ethanoate.

2 **a** State the name of the reagent required to convert propanoic acid to propanamide.

  b Write an equation for the reaction, using structural formulas.

  c Outline one chemical property that differs for propanoic acid and propanamide.

3 Draw the structural formula of the ester obtained from each combination:

  a $CH_3COOH + CH_3OH$

  b $C_6H_5OH + CH_3CH_2COOH$

  c $CH_3CH_2COOH + CH_3CH_2OH$

4 Draw the structural formula of the amide obtained from each combination:

  a $CH_3COOH + CH_3NH_2$

  b $CH_3CH_2COOH + (CH_3)_2NH$

  c NH_3 and CH_3CH_2COOH

5 State the names, and draw the structural formulas of the alcohols and carboxylic acids used to prepare these compounds.

  a Ethyl methanoate

  b Methyl propanoate

  c Propyl methanoate

6 State the names, and draw the structural formulas of the amines and carboxylic acids used to prepare these compounds.

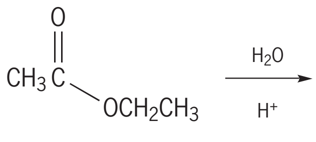
  a Methanamide

  b *N*-ethylpropanamide

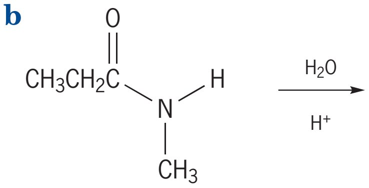
  c *N*,*N*-dimethylethanamide

7 Draw structural formulas for the organic products of the following hydrolysis reactions.

a



b



c $CH_3CH_2Cl \xrightarrow[OH^-]{H_2O}$

8 The side groups of two amino acids are shown in the table below.

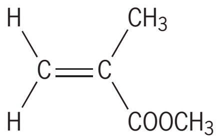
Amino acid	Side-group
Serine	$-CH_2OH$
Valine	$-CH(CH_3)_2$

Draw two possible products of the condensation reaction between serine and valine.

9 Describe the essential difference between the structures of monomers that form addition polymers and the structures of monomers that form condensation polymers.

10 Draw a section of the polymer that forms from each of these monomers.

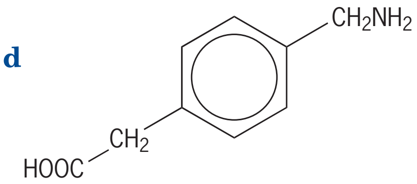
a



b $HOCH_2CH_2COOH$

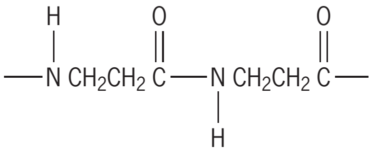
c HOOC—△—COOH and HO—■—OH

d



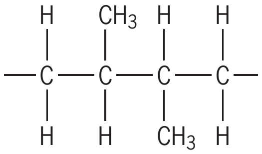
11 Draw structural formulas for the monomers from which each of the following polymers was made.

a

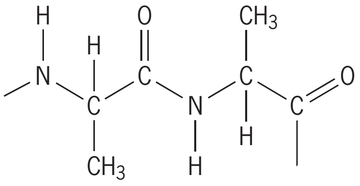


$$-\overset{\overset{H}{|}}{N}CH_2CH_2\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}CH_2CH_2\overset{\overset{O}{\|}}{C}-$$

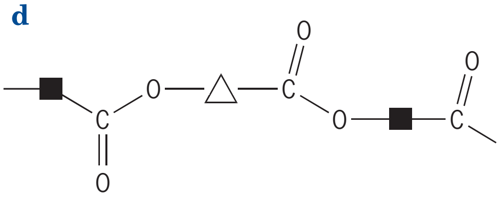
b



c



d



12 Proteins are natural polymers.

a State one way in which a protein is similar to the synthetic polymer nylon.

b State one difference between proteins and nylon.

9.6 REACTION PATHWAYS

To summarize the reactions discussed in this chapter we may construct a 'web' of **reaction pathways**, as shown in figure 9.6.1. You should be able to apply these reactions to any of the hydrocarbons with up to six carbon atoms in their chain.

AS 20.5.1
Deduce reaction pathways given the starting materials and the product. © IBO 2007

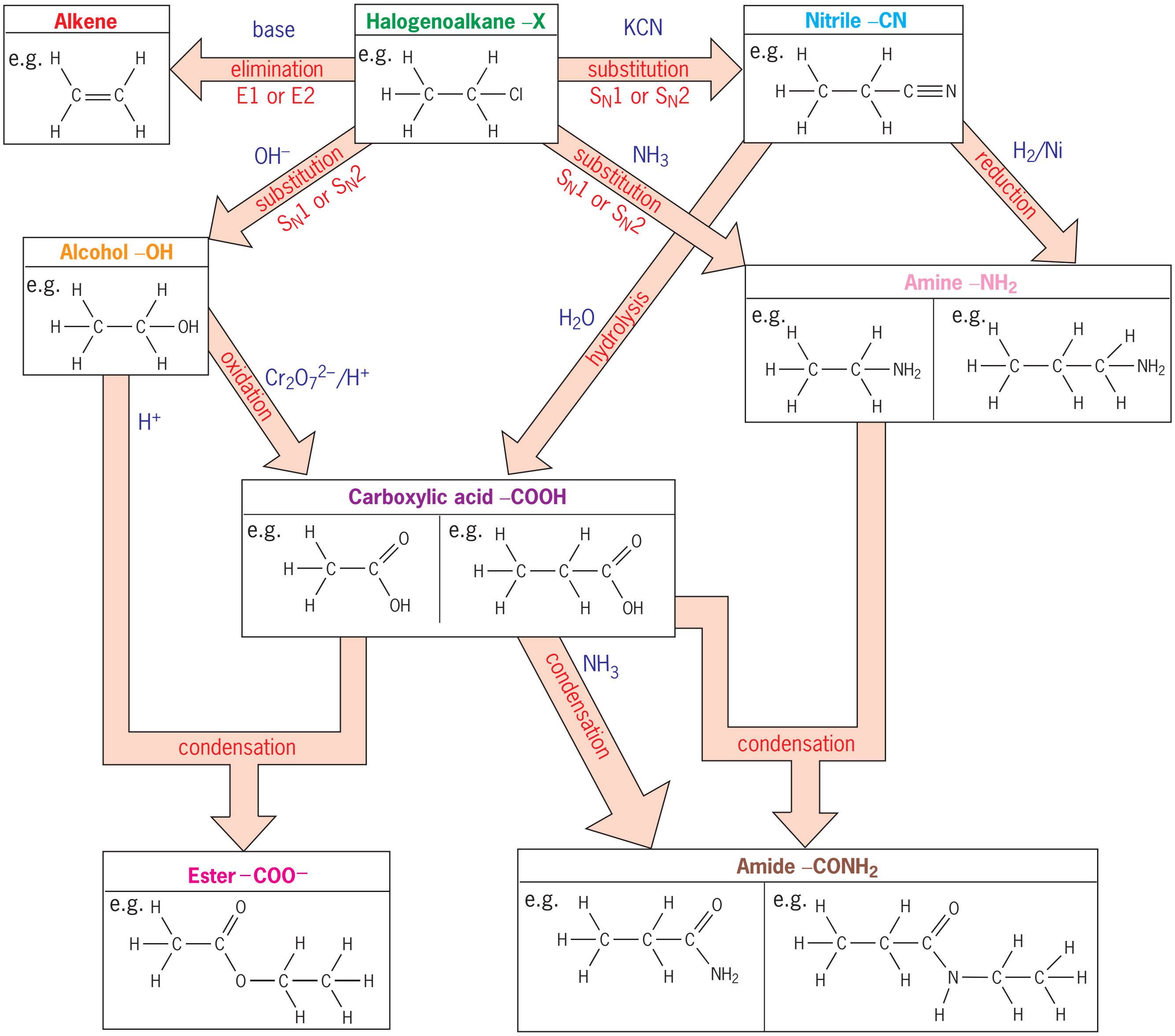


Figure 9.6.1 A 'web' of reaction pathways.

THEORY OF KNOWLEDGE

The disease pernicious anaemia occurs when the body cannot properly absorb vitamin B_{12}, causing the number of red blood cells to drop to fatal levels. Pernicious anaemia was first described in 1821, but for a hundred years scientists could not figure out how to cure it. This all changed in the 1920s, when American pathologist George Whipple found there was regeneration of red blood cells when dogs with a low red cell count were fed large amounts of liver. Whipple's observations were verified in 1926 by American physicians George Minot and William Murphy, who observed that humans suffering from pernicious anaemia were cured after eating large amounts of liver. Whipple, Minot and Murphy shared the 1934 Nobel Prize for their work.

An intensive search then began for the active compound in liver, involving many scientists from the United States and England. In 1948 it was finally isolated in crystalline form and named vitamin B_{12}. Crystals were then given to Dorothy Hodgkin at Oxford University in England, and using a new technology called X-ray diffraction Hodgkin and her team were able to determine its structural and empirical formulas. The structure of a molecule of this size had never been determined before, and there were many chemical and technological problems that had to be overcome during this groundbreaking work, which won her the Nobel Prize for Chemistry in 1964.

It took 11 years for American chemist Robert Woodward to prepare vitamin B_{12} using chemical methods. More than 90 separate reactions were needed to place every group, and every atom in its proper position. In 1965 he won the Nobel Prize in Chemistry for this achievement.

- Why do you think three separate Nobel Prizes were awarded for the discovery, structural determination and synthesis of vitamin B_{12}?
- Why is it important that scientists from different countries and research organizations collaborate and communicate with one another effectively during research?
- Robert Woodward's Nobel Prize was for 'his outstanding achievements in the art of organic synthesis'. Considering that three possible criteria for identifying art are: the intentions of the artists, the quality of the work and the response of the spectators, can the synthesis of vitamin B_{12} be considered a work of art?
- The structural determination of a large molecule such as vitamin B_{12} would not have been possible without the use of technology. What are the implications of this for the advancement of medical science?
- Whipple, Minot and Murphy used inductive reasoning to conclude that a compound in liver could cure pernicious anemia. This can be demonstrated using a simple argument:

  Patient A ate liver and was cured of pernicious anemia.
  Patient B ate liver and was cured of pernicious anemia.
  Patient C ate liver and was cured of pernicious anemia.

  Therefore eating liver is a cure for pernicious anemia.

a Identify some the problems of relying too heavily on the conclusions drawn from inductive reasoning.

b Their conclusion did turn out to be very reliable. What do scientists do to improve the certainty of the conclusions drawn from research?

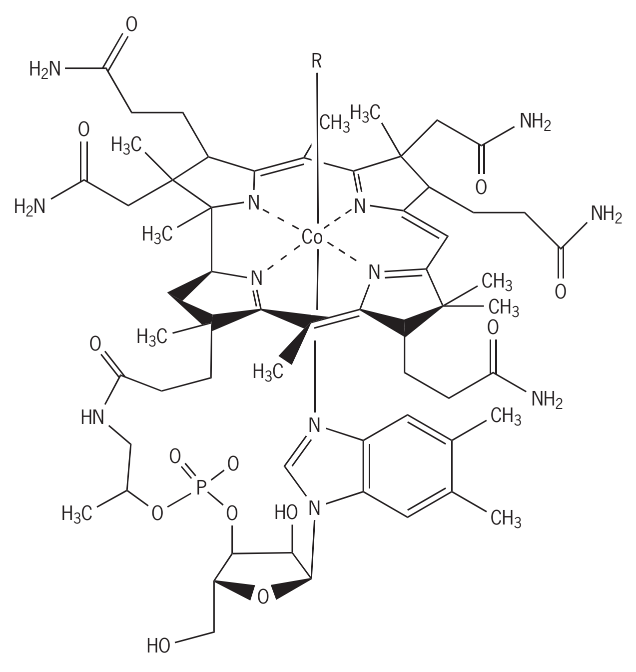


Figure 9.6.3 Vitamin B_{12}.

Worked example 1

Show a reaction pathway for the two-step conversion of 1-bromopropane to 1-butanamine.

Solution

Notice that the conversion involves an increase in chain length by one carbon atom (from prop = 3 to but = 4). Recall that increasing chain length can be done using a nitrile reaction. A suitable pathway is shown below.

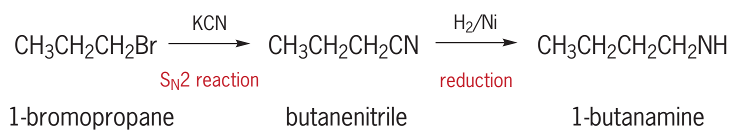


Figure 9.6.2 A reaction pathway for the conversion of 1-bromopropane to 1-butanamine.

In practice, many organic syntheses do not proceed by a simple, short pathway. Often many steps are involved. In developing a multi-step organic synthesis, reaction mechanisms are a powerful tool. They aid in understanding how known reactions proceed, and provide a guide to the conditions that will favour the formation of a desired product. The synthesis of the vitamin B_{12} molecule involved some 90 separate reactions—an impressive example of the art of organic synthesis.

Section 9.6 Exercises

Draw possible two-step reaction pathways for the synthesis of the following compounds from the given starting compounds. Include semi-structural or condensed formulas, and any inorganic reagents and conditions needed for the pathway.

a Ethyl ethanoate from ethanol

b Dimethylamine from methanol

c 1-Propanamine from 1-bromoethane

d Propanenitrile from ethane

e Butanamide from 1-butanol

9.7 ISOMERS—THE SAME BUT DIFFERENT

AS 20.6.1
Describe stereoisomers as compounds with the same formula but different arrangements of atoms in space. © IBO 2007

In the Standard Level course we saw that the alkane butane, C_4H_{10}, could exist in two different structural forms: butane and methylpropane. Similarly, pentanol, $C_5H_{11}OH$, had a variety of possible structures. Molecules that had the same molecular formula but differed in their structural arrangement of atoms were termed structural isomers. The structural isomers seen in alkanes and other homologous series are but one type of isomerism. We now turn our attention to **stereoisomers**—molecules with the same molecular formula and structural formula, but with different spatial arrangements of atoms. Two types of stereoisomers occur: geometric and optical.

Geometric isomers

AS 20.6.3
Describe and explain geometrical isomerism in C3 and C4 cycloalkanes. © IBO 2007

Geometric isomers are the result of inflexibility in bonds. This inflexibility, or restricted rotation, results in different possible arrangements of atoms in space. It is common in both cycloalkanes and alkenes.

Cycloalkanes are generally less flexible than their open-chain counterparts. In propane, for example, rotation is possible around the carbon–carbon bond. In contrast there is no such freedom of rotation in cyclopropane because of geometric constraints. Cyclopropane is a rigid, planar molecule. No bond rotation can take place around the carbon–carbon bond without breaking open the ring—the geometry constrains the molecule.

QuickTime Video
Isomerism

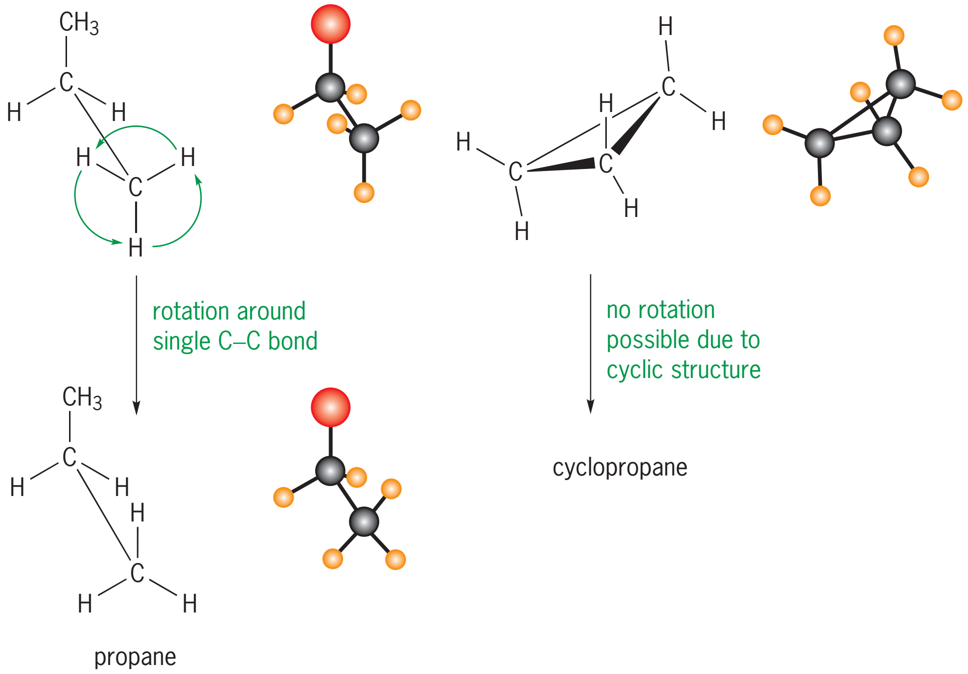


Figure 9.7.1 Propane molecules show rotation around the carbon–carbon bond. Rotation is not possible in cyclopropane without breaking a bond.

Other common ring structures, for example cyclobutane, cyclopentane and cyclohexane, are all severely constrained in their molecular movements. Because of their cyclic nature and these rotational constraints, cycloalkanes have two 'sides', a top and a bottom. This leads to the possibility of isomerism in substituted cycloalkanes. For example, 1,2-dichlorocyclopropane exists as two isomers. These are termed *cis* (from the Latin meaning 'on the same side') and *trans* (from the Latin meaning 'across') isomers, depending on whether the two chlorine atoms are both on top of the ring, or on opposite sides of the ring.

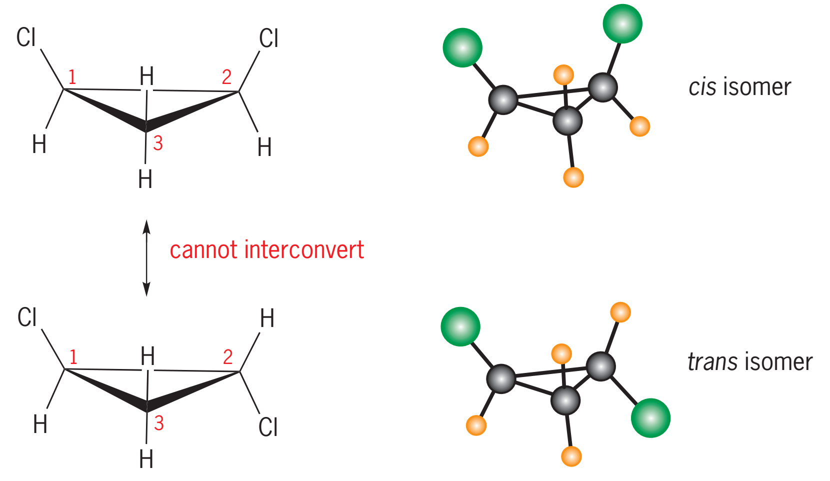


Figure 9.7.2 Geometric isomerism in 1,2-dichlorocyclopropane.

Notice that the two isomers have the same atoms connected in the same order. They differ only in the spatial arrangement of the atoms. These are stereoisomers. This type of *cis–trans* isomerism is common in substituted cycloalkanes.

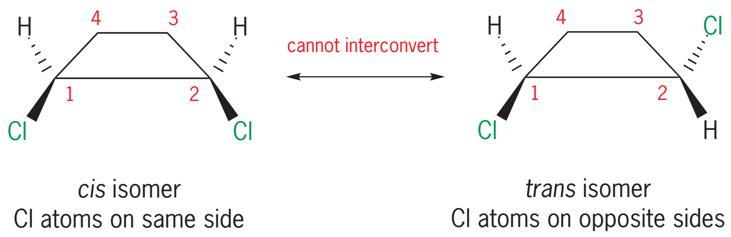


Figure 9.7.3 Geometric isomerism in 1,2-dimethylcyclobutane.

Cis–trans isomerism in cycloalkanes is the result of a lack of rotation around carbon–carbon bonds. This lack of rotation also occurs at the C=C bond in alkenes, giving rise to the possibility of *cis–trans* isomerism in substituted alkenes. For example, 1,2-dichloroethene exists as two geometric isomers. In the *cis* form the two chlorine atoms are on the same side of the double bond; in the *trans* form they are on opposite sides. Another example is that of the *cis* and *trans* isomers of 2-butene, shown in figure 9.7.4. We can see that the *cis* and *trans* forms of 2-butene are different in their spatial arrangement of the methyl groups. How does this influence the chemical and physical properties of the compounds? Do the two geometric isomers exist in equal proportions?

AS 20.6.2
Describe and explain geometrical isomerism in non-cyclic alkenes. © IBO 2007

Interactive CW Animation
Geometric isomers

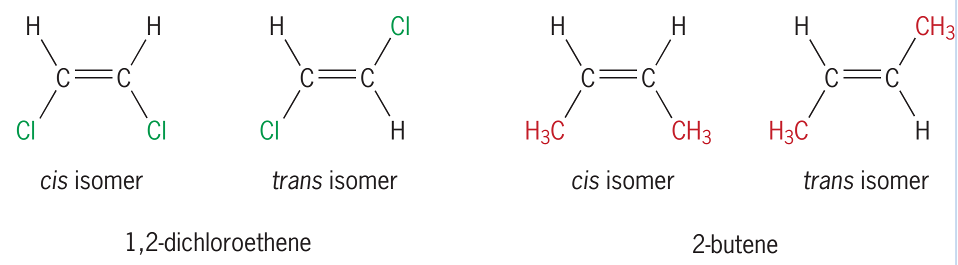


Figure 9.7.4 Geometric isomerism in 1,2-dichloroethene and 2-butene.

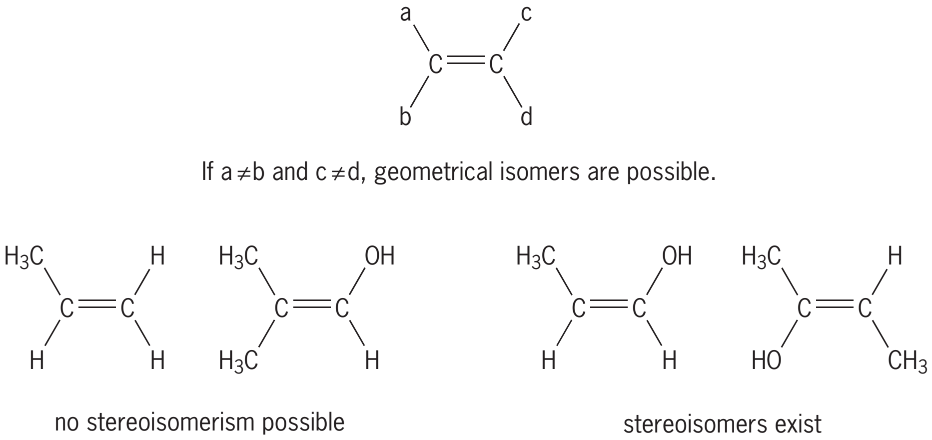


Figure 9.7.5 When do geometric isomers occur? The compound $abC{=}Ccd$ will exist as two geometric isomers as long as $a \neq b$ and $c \neq d$.

AS 20.6.4
Explain the difference in the physical and chemical properties of geometrical isomers. © IBO 2007

If the *cis* and *trans* forms of 2-butene are interconverted (by treatment with a strong acid catalyst) and allowed to reach equilibrium, the *trans* isomer is found to be present at approximately three times the concentration of the *cis* isomer. In other words, the *trans* isomer is more stable. We can account for this in terms of the influence of steric hindrance. When the bulkier methyl groups are on the same side of the double bond, there is strain as both groups try to occupy the same space. This overlap and strain does not occur in the more stable *trans* form, in which the methyl groups are on opposite sides of the double bond.

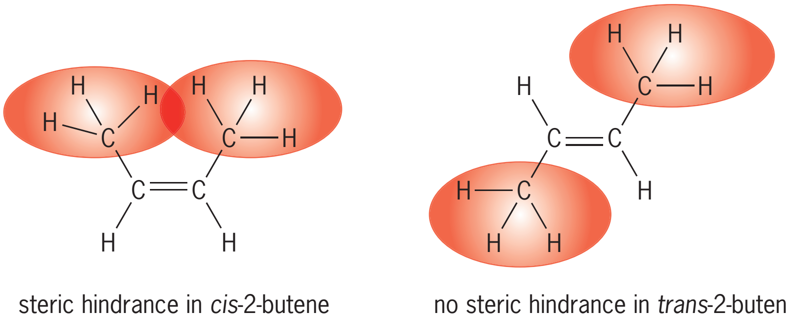
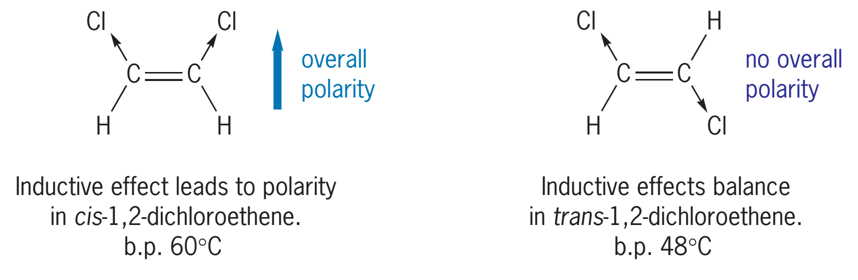


Figure 9.7.6 Steric hindrance in *cis*-2-butene leads to a less stable geometric isomer.

Geometric isomers differ in their physical and chemical properties, sometimes marginally, but often significantly. Several steric hindrance and inductive effects may be involved, so explaining differences is not always straightforward. We will consider several examples to illustrate these effects. Consider again *cis* and *trans* 2-butene. In the *trans* isomer the two bulky groups on the opposite sides of the double bond create a more regular, symmetrical structure than in the less stable *cis* form. The *trans* molecules can pack more tightly and so the intermolecular van der Waals' forces are stronger, leading to the higher melting point for the *trans* isomer.

Consider *cis* and *trans* 1,2-dichloroethene. Here the substituent Cl atoms exert inductive effects on the double bond. The Cl group withdraws electrons. In the *cis* form this withdrawal occurs on the same side of the molecule, leading to an overall polarity. The dipole–dipole attraction between molecules leads to a higher boiling point for the *cis* form. In the *trans* form the inductive effects on opposite sides of the molecule cancel each other. Intermolecular bonding is therefore primarily by van der Waals' forces, resulting in a lower boiling point for the *trans* form.

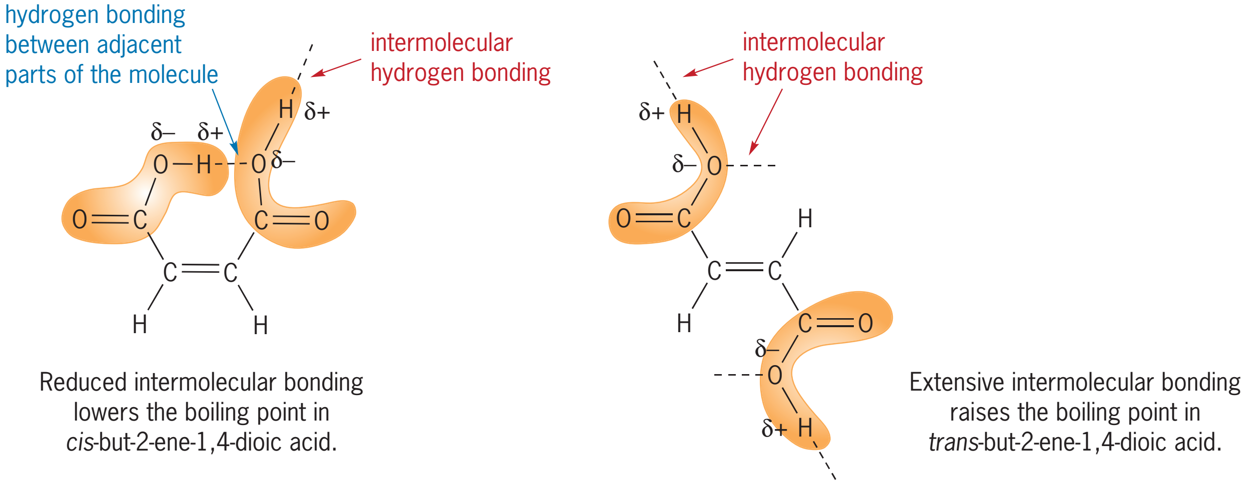


Inductive effect leads to polarity in *cis*-1,2-dichloroethene. b.p. 60°C

Inductive effects balance in *trans*-1,2-dichloroethene. b.p. 48°C

Figure 9.7.7 Inductive effects can be used to explain differences in the boiling points of *cis* and *trans* 1,2-dichloroethene.

The *cis*–*trans* differences are sometimes even more marked. Consider *cis* and *trans* but-2-ene-1,4-dioic acid. In the *cis* form, due to the close proximity of the carboxyl groups on the same side of the double bond, hydrogen bonding between adjacent functional groups within the molecule occurs. This results in reduced intermolecular bonding, decreasing the boiling point considerably. In contrast, the *trans* isomer shows extensive intermolecular hydrogen bonding, resulting in a much higher boiling point.



Reduced intermolecular bonding lowers the boiling point in *cis*-but-2-ene-1,4-dioic acid.

Extensive intermolecular bonding raises the boiling point in *trans*-but-2-ene-1,4-dioic acid.

Figure 9.7.8 Differences in intermolecular bonding can be used to explain differences in the boiling points of *cis* and *trans* but-2-ene-1,4-dioic acid.

The isomers of but-2-ene-1,4-dioic acid also differ considerably in their response to heating. On heating to 150°C the *cis* isomer loses water readily to produce an acid anhydride. In the *trans* form the two carboxyl groups are too far apart to form this cyclic anhydride. The *trans* isomer will only produce the anhydride at the much higher temperature of 250°C. This higher temperature is needed to break the double bond between the carbon atoms and allow rotation about the single bond formed. Following this rotation the two carboxyl groups can react to form the cyclic anhydride.

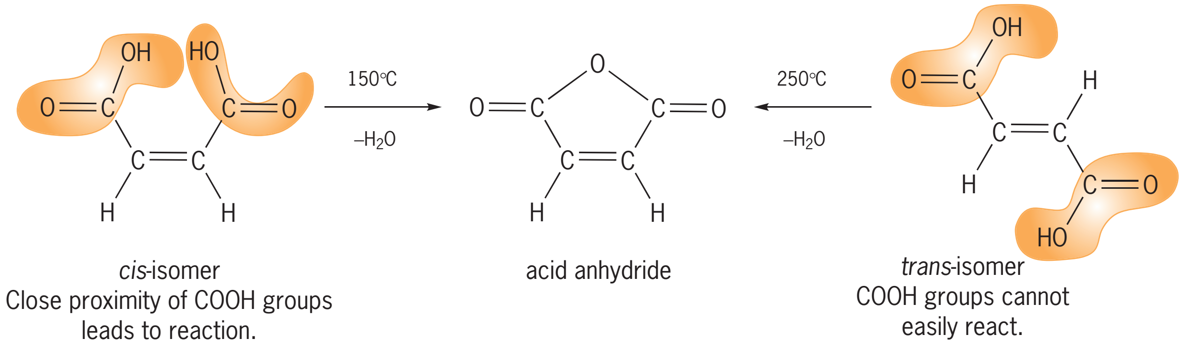


Figure 9.7.9 Differences in spatial arrangement of functional groups leads to different chemical properties in *cis* and *trans* but-2-ene-1, 4-dioic acid.

Optical isomers

AS 20.6.5 Describe and explain optical isomerism in simple organic molecules. © IBO 2007

PRAC 9.3
Modelling stereoisomers

QuickTime Video
Chirality

Consider your hands. How is your right hand like your left hand? How are they different? Clearly your two hands are not identical—they are mirror images of each other, and the left hand cannot be superimposed on the right hand; that is, they cannot be placed on top of one another so that they match exactly. Try it for yourself by holding your right hand up to a mirror. Which hand does the image look like? Think about how handedness plays a role in your daily activities. With which hand do you write, play an instrument or use a piece of sporting equipment? Are you 'left handed' or right handed?

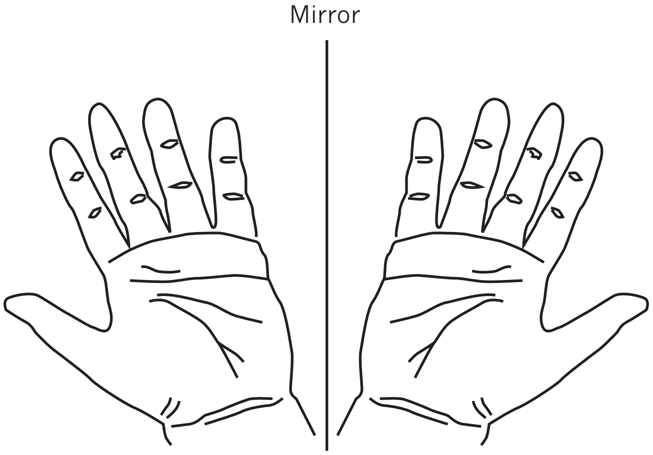


Figure 9.7.10 Your left and right hands are mirror images. One hand cannot be superimposed on the other.

The idea of handedness also applies to many organic molecules. In particular it applies to those molecules based on a carbon atom with four different substituents tetrahedrally arranged around it. Like your left and right hands, molecules of the formula CWXYZ form mirror images that are not superimposable.

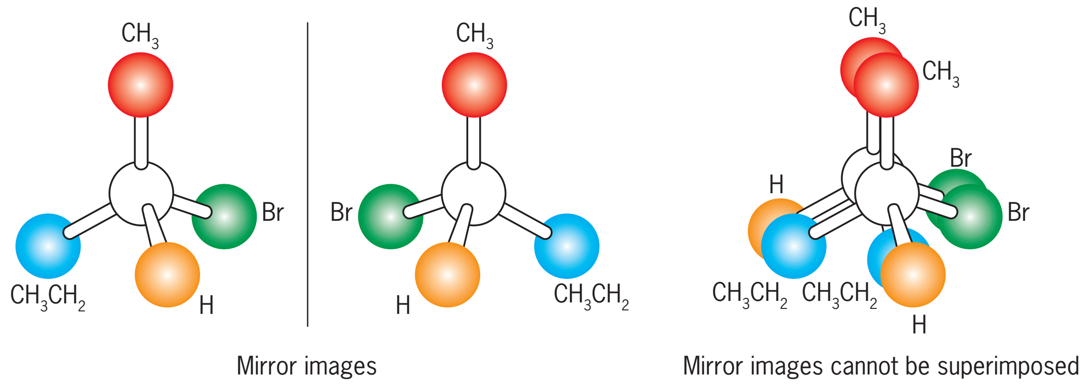


Figure 9.7.11 Some molecules are not superimposable on their mirror image.

Molecules that are not identical to their mirror image are called **enantiomers** (from the Greek *enantio* meaning 'opposite'). Enantiomers are related in the way your left and right hands are related. No matter how hard you try you cannot superimpose one on the other. Enantiomers are said to be **chiral** (from the Greek *cheir* meaning 'hand'). A chiral molecule and its mirror image cannot be placed so they match exactly. To predict whether a molecule is chiral we must look for a plane of symmetry—a plane through the molecule such that one half of the molecule is the mirror image of the other half. A molecule with such a plane of symmetry cannot be chiral, and so must be *achiral*.

The most commonly encountered cause of chirality is the molecule containing a carbon atom bonded to four different substituents, CWXYZ. Such a carbon is called an asymmetric centre, and can also be referred to as a chiral carbon. Molecules containing asymmetric carbon atoms are chiral molecules. The asymmetric carbon atom is sometimes indicated using an asterisk. Typical molecules containing asymmetric carbon atoms are shown in figure 9.7.12.

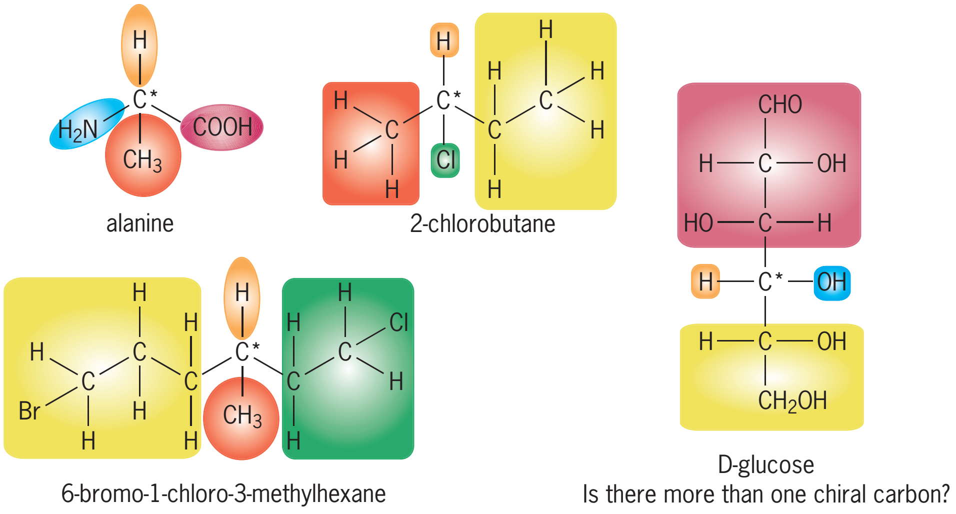


Figure 9.7.12 Chiral molecules containing asymmetric carbon atoms (indicated by an asterisk *). The asymmetric carbon atom is bonded to four different substituents, indicated here by four shaded areas.

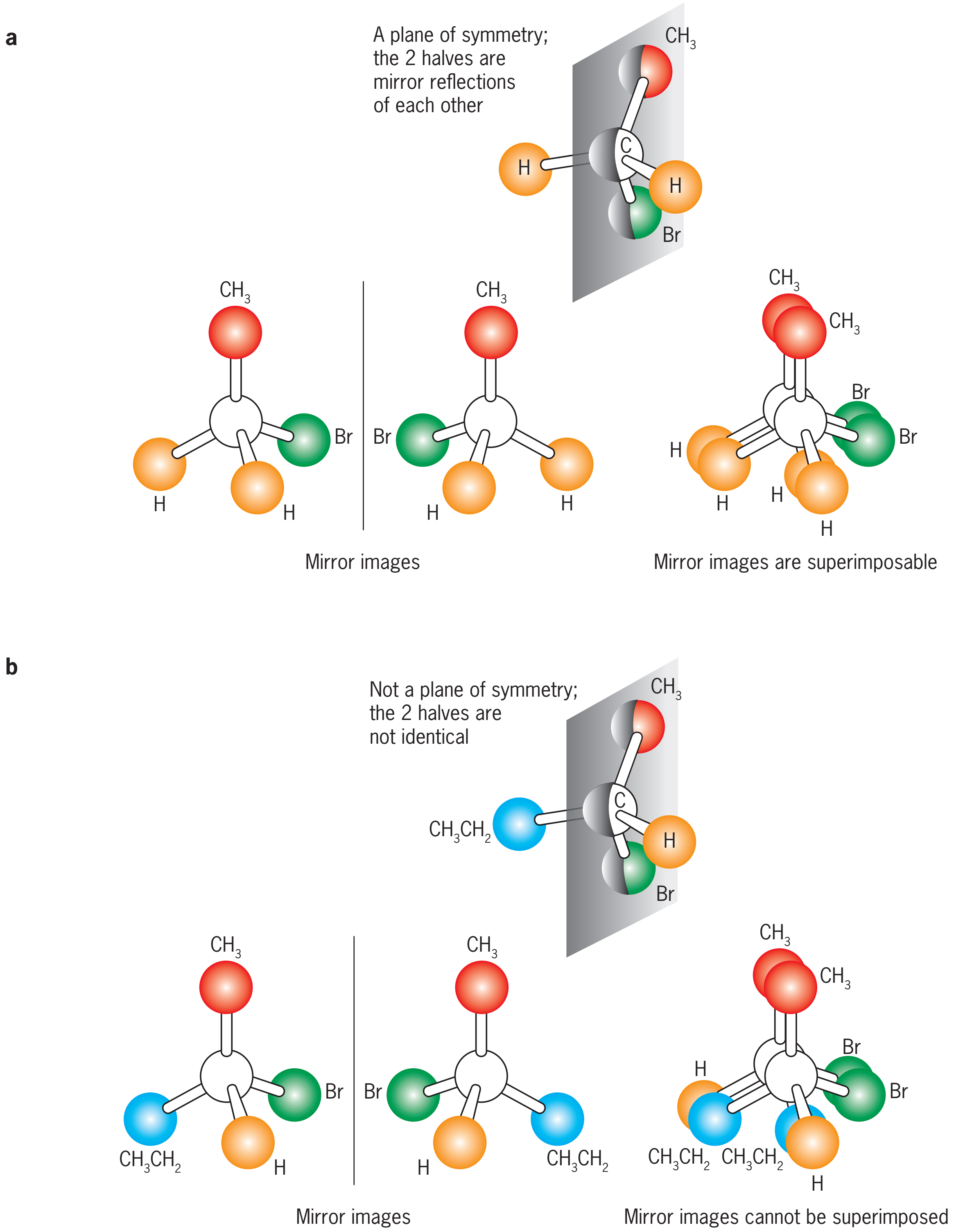


Figure 9.7.13 (a) Molecules with a plane of symmetry are superimposable on their mirror image. They are achiral. (b) Molecules without a plane of symmetry are not superimposable on their mirror image. They are chiral.

AS 20.6.7
Compare the physical and chemical properties of enantiomers. © IBO 2007

How do the physical properties of enantiomers compare? The physical properties such as melting point, solubility, density and spectroscopic properties of enantiomers are identical. Only one physical property differs between enantiomers—their direction of rotation of plane-polarized light. What is this property and why is it important?

A beam of white light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of travel of the light. When this beam of light is passed through a polarizer (which acts somewhat like a gate) only waves oscillating in a single plane pass through it. The emerging light is called **plane-polarized light**. Waves in all other planes are blocked.

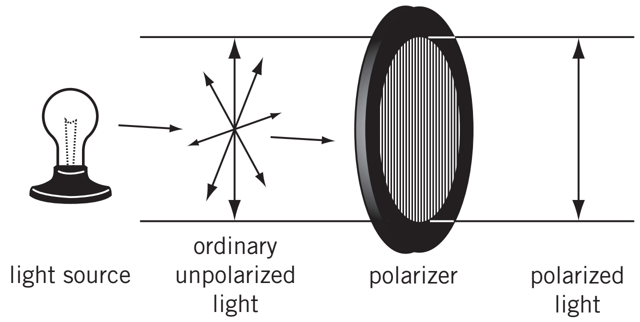


Figure 9.7.14 In plane-polarized light the oscillation of the light occurs in a single plane.

The French scientist Jean Baptiste Biol (1774–1862) was one of the first to notice that when a beam of plane-polarized light passed through a solution of certain organic compounds the plane of polarization was rotated. Only some organic compounds exhibit this property. Those that do are called optically active. Investigation of this rotation effect is conducted using a **polarimeter** (schematically shown in figure 9.7.15). Plane-polarized light is passed through a tube containing a solution of the optically active organic compound. Rotation of the light occurs. The light then passes to a second polarizer—the analyser. By rotating the analyser until the light passes through it, the new plane of polarization can be found. The extent of rotation is then measured as the angle (θ) between the original and rotated planes of light.

20.6.6
Outline the use of a polarimeter in distinguishing between optical isomers.
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Optical activity

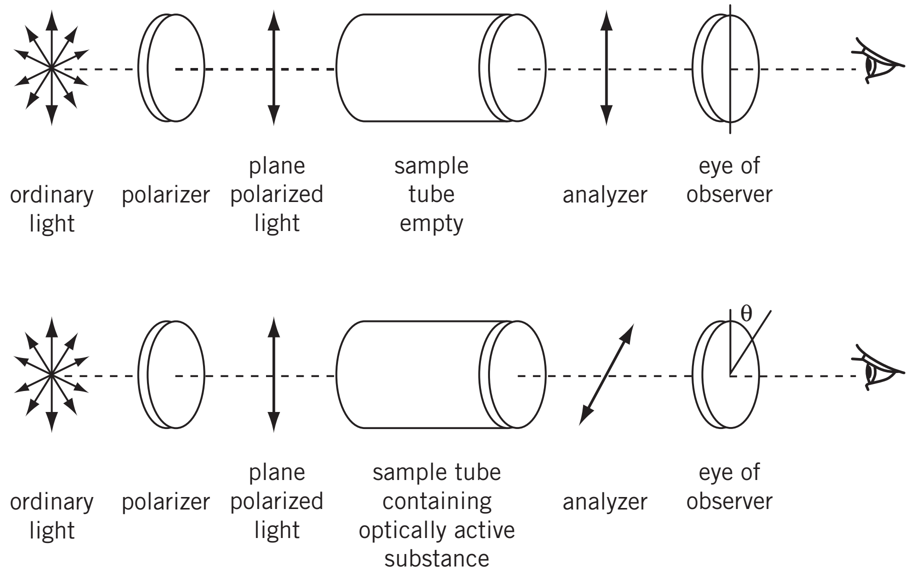


Figure 9.7.15 Schematic diagram of the operation of the polarimeter.

Optically active compounds that rotate light clockwise (i.e. to the right), are said to be **dextrorotatory** (from the Latin *dextro* meaning 'right'). Those that rotate light counterclockwise, to the left, are said to be **levorotatory** (from the Latin *levo* meaning 'left'). By convention, rotation to the right is given a plus sign (+), while rotation to the left is given a minus sign (–). For example, (–)morphine is levorotatory, while (+)sucrose is dextrorotatory. Enantiomers rotate plane-polarized light to the same extent, but in opposite directions. One is therefore the (–) or l-form, the other the (+) or d-form. If a solution contains a 50:50 mixture of enantiomers, the solution will be optically inactive. Such a mixture is called a **racemic mixture** or **racemate**. Racemic mixtures show zero optical activity because the rotation from one enantiomer exactly cancels the opposite rotation by the other enantiomer.

THEORY OF KNOWLEDGE

The Greek scholar Socrates (469–399 BC) was well known for his questioning skills, which became known as the Socratic method. His method involved asking students for the definition of a concept, and if their answers were uncertain or ambiguous he encouraged them to deepen their enquiry. Today we call this critical thinking. Plato (428–347 BC) was a student of Socrates and founded the first university—the Academy in Athens—which specialized in the advancement of knowledge in the areas of mathematics, science and logic. The way of knowing taught at the Academy was called 'knowledge by description' or 'propositional knowledge'. In order for a claim to be called knowledge it had to pass three tests. It had to be believed, the belief had to be true and the true belief had to be justified. In other words, knowledge was defined as a justified true belief. This definition of knowledge is still useful today, even though it has been challenged by some philosophers.

So how do we know that optical isomers exist if we cannot see their enantiomeric forms? Well, first we need to believe that they exist and second we need to provide justification for our belief. Observing how some organic molecules can rotate plane-polarized light while others cannot provides very useful indirect evidence that can be used to deduce the asymmetric structure of optically active molecules and how they might be represented. It can also help to explain their chemical properties. The value of indirect evidence is that it expands what chemists know about these molecules by providing further justification for believing the claim. Being able to observe for one's self some natural phenomenon is an important part of the processes of justifying scientific beliefs. Without the ability to directly observe the arrangement of atoms on a molecular scale, observing the behaviour of optical isomers provides worthwhile indirect evidence to support their existence.

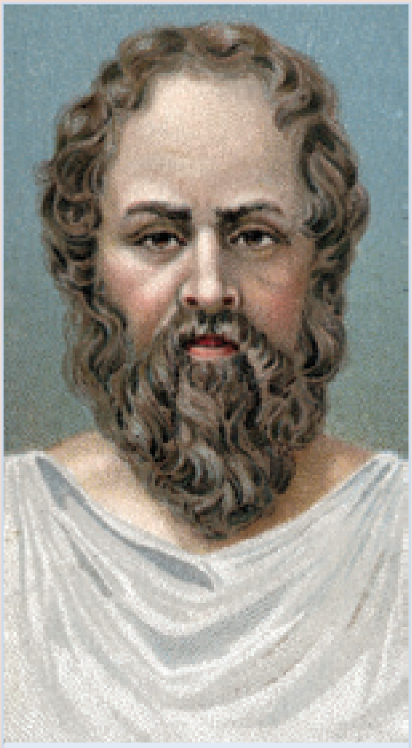


Figure 9.7.16 The Greek scholar Socrates.

WORKSHEET 9.4
Stereoisomers

Interactive CW Animation
Enantiomers of alanine

How do the chemical properties of enantiomers compare? As for their physical properties, the chemical properties of enantiomers are identical except for one—their interaction with other optically active compounds. For example, in the human body different enantiomers may have completely different physiological effects. Biological systems involve the interaction of molecules, and are particularly sensitive to molecular shape. Different enantiomers may therefore have completely different effects due to their difference in shape. For example, l-aspartame tastes sweet, while d-aspartame tastes bitter. The d-glucose isomer is sweet and nutritious and is an important component of our diet, while l-glucose is tasteless and cannot be metabolized by the body. These substances have different tastes because taste is the result of interactions between these chiral molecules and chiral receptors in the taste buds of your mouth. The d-form of lactic acid is produced by muscle tissue in humans, while the l-form is found in sour milk. In fact, in many biological systems one enantiomer is found almost exclusively. Thus most amino acids occur in the l-form, while most sugars occur in the d-form.

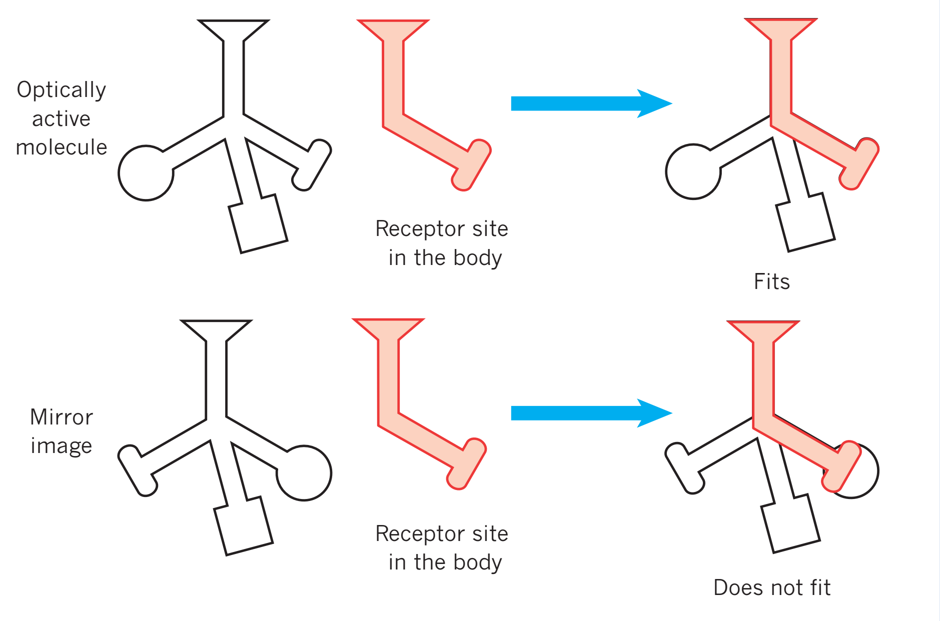


Figure 9.7.17 Schematic diagram to explain the different effects of enantiomers in biological systems.

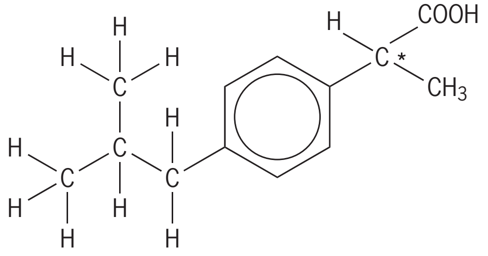
CHEM COMPLEMENT

Optically active drugs

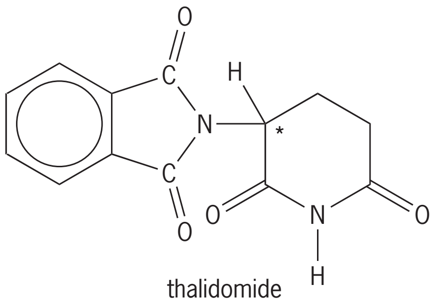
The thousands of different drugs in use worldwide come from a variety of sources. Many drugs are isolated directly from plants and bacteria. Others are made by chemically modifying naturally occurring compounds, and some are completely synthetic. Drugs that come from natural sources, either directly or by modification, are usually chiral, and are often found as a single enantiomer. Racemic mixtures are rare. In contrast, entirely synthetic drugs are either achiral, or are produced as a racemic mixture of two enantiomers. For example, ibuprofen, used as a mild pain reliever, contains one asymmetric carbon atom and so is chiral. Ibuprofen is produced and sold as a racemic mixture, even though only one enantiomer has an analgesic effect. The other enantiomer is biologically inactive.

It is chemically (and economically) wasteful to synthesize and administer enantiomers that do not have the desired pharmacological effect. Perhaps, more importantly, examples are known where the presence of the 'inactive' enantiomer in a racemic mixture alters or reduces the pharmacological effect of the 'active' enantiomer. For example, ibuprofen in a racemic mixture is slower to act than the 'active' enantiomer alone.

In other cases the presence of the 'inactive' enantiomer leads to unexpected, and unwanted effects. One example is the tragic case of thalidomide. Molecules of this drug have an asymmetric carbon atom and so are chiral, existing as two enantiomers. In 1957 the racemic mixture was sold in Europe as a sleeping pill and tranquilizer. Many pregnant women took the drug to alleviate 'morning sickness'. However, a major side effect became apparent as many women gave birth to deformed babies, large numbers of whom lacked correctly formed limbs. In 1961 thalidomide was removed from the market. Some years later, experiments with rats suggested that it was one enantiomer that produced the deforming effects; the other enantiomer produced the desired effects.



ibuprofen



thalidomide

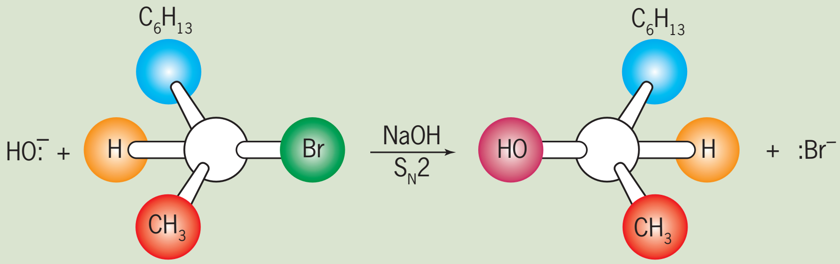
Figure 9.7.18 Ibuprofen and thalidomide. Both are optically active as they have an asymmetric carbon atom. Only one enantiomer of each displays the desired pharmacological effects.

CHEM COMPLEMENT

Stereochemical evidence

We have considered the existence of **optical isomers**, and looked at the cause of this isomerism and its effects on the properties of molecules. We turn now to a ‘use’ of our understanding of optical isomerism. Consider again the nucleophilic substitution reactions covered in section 9.3. When 2-bromooctane reacts with sodium hydroxide under appropriate conditions, an S_N2 reaction occurs to produce 2-octanol. Both the reactant and the product of this reaction are chiral. Their molecules contain an asymmetric carbon atom and so they both exist as optical isomers. Analysis of the reactants and products of the substitution reaction being considered show that if the reactant is the (–) enantiomer, the product is the (+) enantiomer. The attacking OH group takes a position opposite to that of the bromide leaving group. An inversion of configuration has occurred.

a

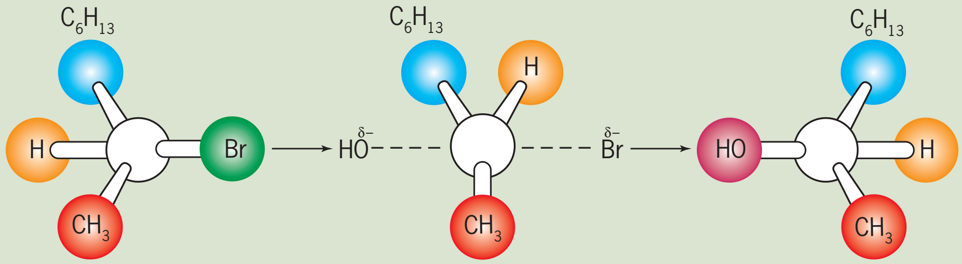


(–) 2-bromooctane

(+) 2-octanol

The explanation lies in the reaction mechanism, in which the attack by the hydroxide nucleophile occurs opposite the bromide leaving group. As the transition state forms, the three bonds on the central carbon atom take up a planar arrangement, and then move to a tetrahedral arrangement opposite their original positions. It is somewhat like what happens when an umbrella is turned inside out on a very windy day. The stereochemistry of the reactants and products supports our ideas of the reaction mechanism being one of a ‘rear end’ attack by the nucleophile.

b



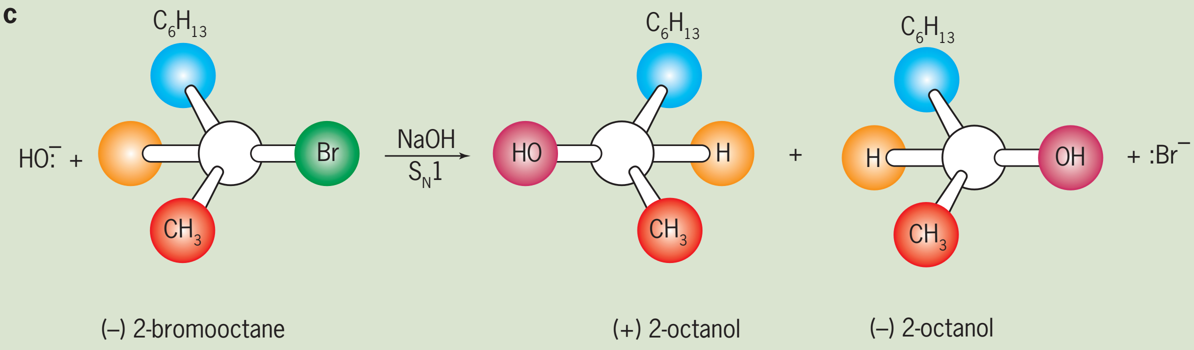
Complete inversion has occurred.

Inversion of configuration usually occurs when chiral molecules react. This fact actually made its discovery difficult.

Paul Walden discovered the inversion phenomenon in 1896, when he looked at one of the reactions that is an exception to the norm, one in which inversion does not take place!

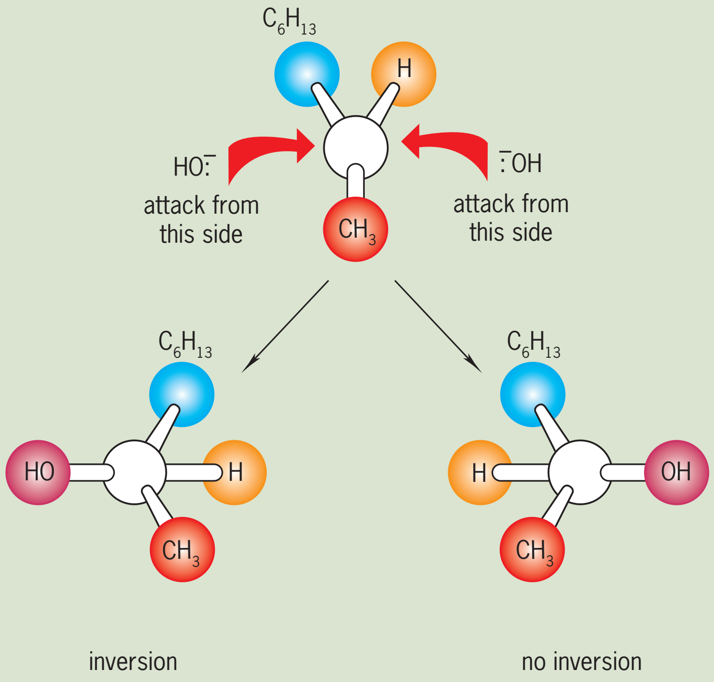
What of the stereochemistry of the S_N1 reaction? When 2-bromooctane reacts with sodium hydroxide under appropriate conditions, an S_N1 reaction can occur to produce 2-octanol. Analysis of the reactants and products of this substitution show that if the reactant is the (–) enantiomer, the product is a mixture of both the (+) and (–) enantiomers.

c



How do we explain this mixture of enantiomers? Consider again the mechanism of carbocation formation. The carbocation has a flat structure. The nucleophile may attack from either side, leading to a mixture of enantiomeric products. Again, the stereochemistry evidence supports the proposed mechanism.

d



This consideration of nucleophilic substitution reaction mechanisms illustrates how an understanding of optical isomers, and the ability to distinguish them using polarimetry, provides evidence of reaction mechanisms that is difficult to obtain by any other means.

Section 9.7 Exercises

1 **a** Define each of the following types of isomers.

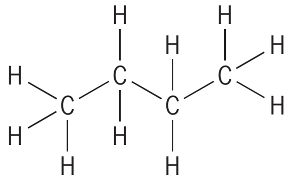
  i Geometric

  ii Optical

  iii Structural

b What type of isomers do each of the following pairs represent?

i



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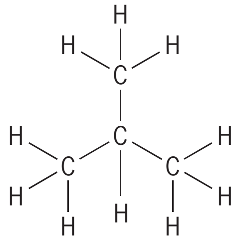
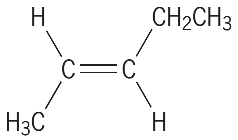


ii



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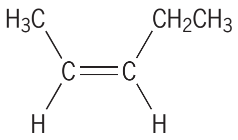
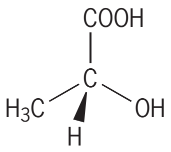


iii



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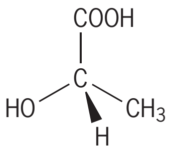


2 Draw the following molecules and place an asterisk at each chiral centre in each molecule.

a $CH_3CH(OH)COOH$

b $CH_3CH_2COOCH(CH_3)CH_2CH_3$

c 2-Chlorobutane

d 2-Methylbutan-1,2-diol

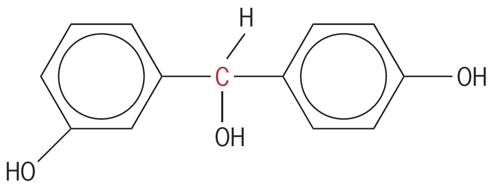
3 Identify which of the following molecules have a chiral carbon shown in red.

I $CH_3CH(OH)CH_2CH_3$

II $CH_3CH_2COCH_2CH_3$

III $CH_3CH_2CH(Br)CH_2CH_3$

IV



4 Draw possible geometric isomers for the following compounds.

a 2-Hexene

b 1,2-Dibromocyclobutane

5 Identify which of the following compounds will show optical activity. Explain your choice.

I 3-Chloropentane

II 1-Chloropentane

III 1-Chloro-2-methylpentane

IV 2-Chloro-2-methylpentane

6 **a** Explain what is meant by the term *plane-polarized light*.

b Describe how optical isomers can be distinguished using a polarimeter.

7 **a** The 2-amino acid alanine found in proteins is chiral. Draw the two enantiomers of alanine.

b Use table 19 of the IB Data booklet to identify the 2-amino acid that does not rotate the plane of polarized light.

8 Compound X exists in two enantiomeric forms, (+)X and (–)X, and in a racemic form (+/–)X.

a Complete the following table showing the physical properties of the enantiomers of X.

Physical property	(+)X	(–)X	(+/–)X
Melting point (°C)	115		<115
Density (g cm^{-3})	0.802		
Rotation of plane-polarized light (°)		–15	

b Suggest why the melting point of the racemic form is lower than that of the (+) form.

9 Consider the alkenes of formula C_5H_9Br.

Draw the structural formula of one alkene of this formula that will show:

a optical isomerism, but not *cis–trans* geometric isomerism

b *cis–trans* geometric isomerism but not optical isomerism

c both *cis–trans* geometric isomerism and optical isomerism

d neither *cis–trans* geometric isomerism nor optical isomerism.

10 Draw structural isomers of $C_5H_{10}O$ which illustrate:

a functional group isomerism

b geometric isomerism

c hydrocarbon chain isomerism

d optical isomerism.

11 Lactic acid can be produced by reaction of propenoic acid and water, or by extraction from milk. How might samples from these two sources differ?

Chapter 9 Summary

Terms and definitions

Amide A functional group considered as a derivative of the carboxylic acid group in which the –OH of the carboxyl group is replaced by $-NH_2$. It is represented as $-CONH_2$.

Amine A functional group made up of a nitrogen atom bonded to two hydrogen atoms. This $-NH_2$ group (known as an amino group) replaces one hydrogen in the structure of an alkane.

Carbocation The positively charged species formed following the heterolytic fission of the C–X bond in a halogenoalkane.

Chiral A chiral molecule and its mirror image cannot be placed so they match exactly. A chiral molecule lacks a plane of symmetry in the molecule. A chiral carbon in a molecule is one that has four different substituents attached.

Condensation polymerization reaction A reaction in which monomers with two functional groups react together in condensation reactions to form a polymer chain.

Condensation reaction A reaction in which two molecules containing functional groups react and join together with the formation of a small molecule (often water).

Dextrorotatory Optically active compounds that rotate light clockwise (to the right) are said to be dextrorotatory. By convention, rotation to the right is given a plus sign (+).

Elimination reaction The removal of a hydrogen halide HX from a halogenoalkane to form an alkene. Occurs in competition with substitution reactions when a halogenoalkane is reacted with a nucleophile.

E1 (unimolecular elimination) An elimination reaction in which the rate of reaction depends on the concentration of the halogenoalkane only: $\text{Rate} = k[\text{RX}]$. In the two-step process a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. A base then removes a hydrogen atom from the carbon atom adjacent to the C–X carbon atom.

E2 (bimolecular elimination) An elimination reaction in which the rate of reaction depends on the concentration of the halogenoalkane and the base (B): $\text{Rate} = k[\text{B}][\text{RX}]$. In the one-step process the base attacks a hydrogen atom on the carbon atom adjacent to the C–X carbon atom, forming a transition state with partially formed C–X, C–H, B–H and C=C bonds.

Enantiomers Isomers that are that not identical to their mirror images; non-superimposable mirror images. Enantiomers rotate plane-polarized light to the same extent, but in opposite directions. One is therefore the (–) or l-form, the other the (+) or d-form.

Geometric isomers Molecules with the same molecular formula and structural formula, but with different spatial arrangements of atoms due to restricted rotation about a double bond or a ring structure.

Heterolytic fission The breaking of a covalent bond in which one of the atoms involved in the bond retains both electrons from the bonds, forming an anion.

Homologous series A family of compounds that share the same general formula.

Levorotatory Optically active compounds that rotate light counterclockwise (to the left) are said to be levorotatory. By convention, rotation to the left is given a minus sign (–).

Nitrile A functional group made up of a carbon atom triple-bonded to a nitrogen atom, represented as –CN; sometimes called cyanides or cyano compounds.

Nucleophile An electron-rich, nucleus-loving species. A reactant with a non-bonding electron pair, or a negative charge that is attracted to a centre of positive charge.

Nucleophilic substitution A substitution reaction in which a nucleophile is attracted to a positively charged centre.

Optical isomers Molecules with the same molecular and structural formulas, but with different spatial arrangements of atoms. Molecules that are not identical to their mirror image. Also known as enantiomers.

Plane-polarized light Light with waves oscillating in a single plane.

Polarimeter A device in which plane-polarized light is passed through a tube containing a solution of an optically active organic compound. Rotation of the light occurs. The light then passes to a second polarizer—the analyser. By rotating the analyser until the light passes through it, the new plane of polarization can be found. The extent of rotation is then measured as the angle (α) between the original and rotated planes of light.

Positive inductive effect The tendency of alkyl groups to 'push' the bonding electron pair towards the carbon of the C–X bond in a halogenoalkane. One effect of electron 'pushing' alkyl groups is to allow the positive charge of the central carbon in the carbocation to be dispersed, and so to be more stabilized.

Racemic mixture or racemate A 50 : 50 mixture of two enantiomers. Racemic mixtures show zero optical activity because the rotation from one enantiomer exactly cancels the opposite rotation by the other enantiomer.

Reaction pathway A series of steps that traces the reaction of a reactant to form a product which it cannot form directly.

S_N1 (unimolecular nucleophilic substitution) A nucleophilic substitution reaction in which the rate of reaction depends on the concentration of one reactant only: Rate = k[RX]. In the two-step process a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. The nucleophile then reacts rapidly with the carbocation.

S_N2 (bimolecular nucleophilic substitution) A nucleophilic substitution reaction in which the rate of reaction depends on the concentrations of both reactants: Rate = k[Nu][RX]. In the one-step process the nucleophile attacks the halogenoalkane, forming a transition state with partially formed C–X and C–Nu bonds.

Stereoisomers Molecules with the same molecular and structural formulas, but with different spatial arrangements of atoms. Two types occur, geometric and optical.

Steric hindrance A change in reactivity due to the spatial arrangement of groups of atoms. It includes the tendency of bulky alkyl groups to crowd the approach of an attacking species, or the crowding by groups of atoms within the same molecule.

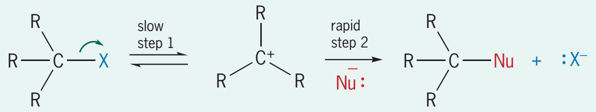
Concepts

- A functional group is an atom or group of atoms attached to a hydrocarbon chain. These functional groups are significant because, to a large extent, they determine the reactivity and chemical properties of the compound. Examples of functional groups and their names are given in the following table.

Functional group homologous series	Condensed structural formula	Suffix or prefix used in naming
Alcohols	R–OH	-ol
Halogenoalkanes	R–X	halo, e.g. chloro-
Aldehydes	R–CHO	-al
Ketones	R–COR′	-one
Carboxylic acids	R–COOH	-oic acid
Amines	RNH_2	amino- or -ylamine or -amine
Nitriles	R–CN	-nitrile
Esters	R–COOR′	R′-yl R-oate
Amides	$R–CONH_2$	-amide

- Synthesis and reactions of amines, nitriles, esters and amides are shown in the table on the next page.
- In nucleophilic substitution of a halogenoalkane (RX), an electron-rich (nucleus-loving) species, the nucleophile (Nu) replaces the halogen in the halogenoalkane. This halogen is displaced and forms a leaving group (X). Nucleophilic substitution occurs by two mechanisms, S_N1 and S_N2.
- S_N1 (unimolecular nucleophilic substitution) reactions display first-order kinetics, in which the rate of reaction depends on the concentration of the halogenoalkane only: Rate = k[RX].

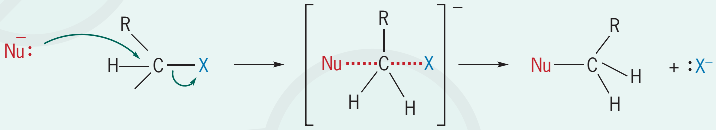
  In the two-step process below a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. The nucleophile then reacts rapidly with the carbocation.



Functional group	Reaction type	Equation	Product
Halogenoalkanes	Nucleophilic substitution with ammonia as the nucleophile	$RX + NH_3 \rightarrow RNH_2 + HX$ $RX + RNH_2 \rightarrow R_2NH \rightarrow R_3N$	Amine
Halogenoalkanes	Nucleophilic substitution with cyanide ion as the nucleophile	$RX + KCN \rightarrow RCN + KX$	Nitrile
Amines	Acid–base	$RNH_2 + H+ \rightarrow RNH_3+$	Weak acid
Nitriles	Acid-catalysed hydrolysis	$RCN \xrightarrow{H_3O^+} RCOOH + NH_3$	Carboxylic acid
Nitriles	Metal-catalysed reduction using hydrogen	$RCN \xrightarrow{H_2/Ni} RCH_2NH_2$	Amine
Carboxylic acid + alcohol	Condensation	$RCOOH + R'OH \rightarrow RCOOR' + H_2O$	Ester
Carboxylic acid + amine	Condensation	$RCOOH + R'NH_2 \rightarrow RCONHR' + H_2O$	Amide

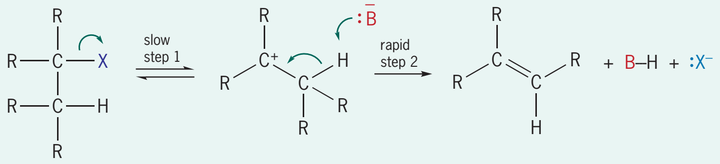
- S_N2 (bimolecular nucleophilic substitution) displays second-order kinetics, in which the rate of reaction depends on the concentration of the halogenoalkane and the nucleophile (Nu): Rate = k[Nu][RX].

  In the one-step process below the nucleophile attacks the halogenoalkane, forming a transition state with partially formed C–X and C–Nu bonds.



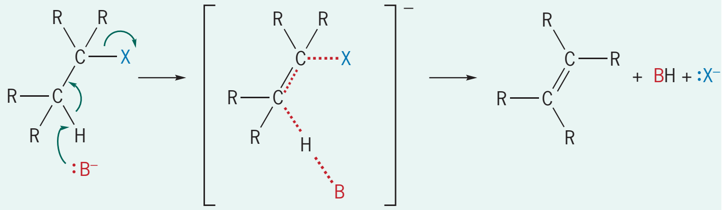
- The factors affecting S_N1 and S_N2 reactions of halogenoalkanes are summarized in the table on the next page.
- The hydrogen halide HX may be removed from a halogenoalkane by an elimination reaction. These elimination reactions from halogenoalkanes are a useful method for preparing alkenes. However, since halogenoalkanes undergo both substitution and elimination reactions when reacted with basic reagents such as OH^-, there will always be competition between the two reactions. Elimination reactions occur by two mechanisms, E1 and E2.
- E1 (unimolecular elimination) displays first-order kinetics, in which the rate of reaction depends on the concentration of the halogenoalkane only: Rate = k[RX].

  In the following two-step process a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. A base then removes a hydrogen atom from the carbon atom adjacent to the C–X carbon atom.



- E2 (bimolecular elimination) displays second-order kinetics, in which the rate of reaction depends on the concentration of the halogenoalkane and the base (B): Rate = k[B][RX].

  In the one-step process below the base attacks a hydrogen atom on the carbon atom adjacent to the C–X carbon atom, forming a transition state with partially formed C–X, B–H, C–H and C=C bonds.



- Factors influencing substitution and elimination reactions are summarized in the table on the next page.
- Polymerization reactions involve the joining together of a large number of small molecules called monomers.
  - In addition polymerization the monomer contains a carbon–carbon double bond.

    For example:

$$nCH_2CH_2 \xrightarrow{\text{high } T \text{ and } P} (CH_2CH_2)_n$$

- In condensation polymerization the monomers must contain two functional groups. Functional groups on adjacent monomers undergo condensation reactions to form an amide or ester linkage.

  For example:

  $$HOCH_2CH_2OH + HOOCC_6H_4COOH \rightarrow -OCH_2CH_2OOCC_6H_4CO-$$

- Various chemical reactions involving organic compounds may combine to produce reaction pathways for the synthesis of a particular organic compound. The reaction sequence shown at the top of the next page is useful for adding a carbon atom to the chain during an organic synthesis.

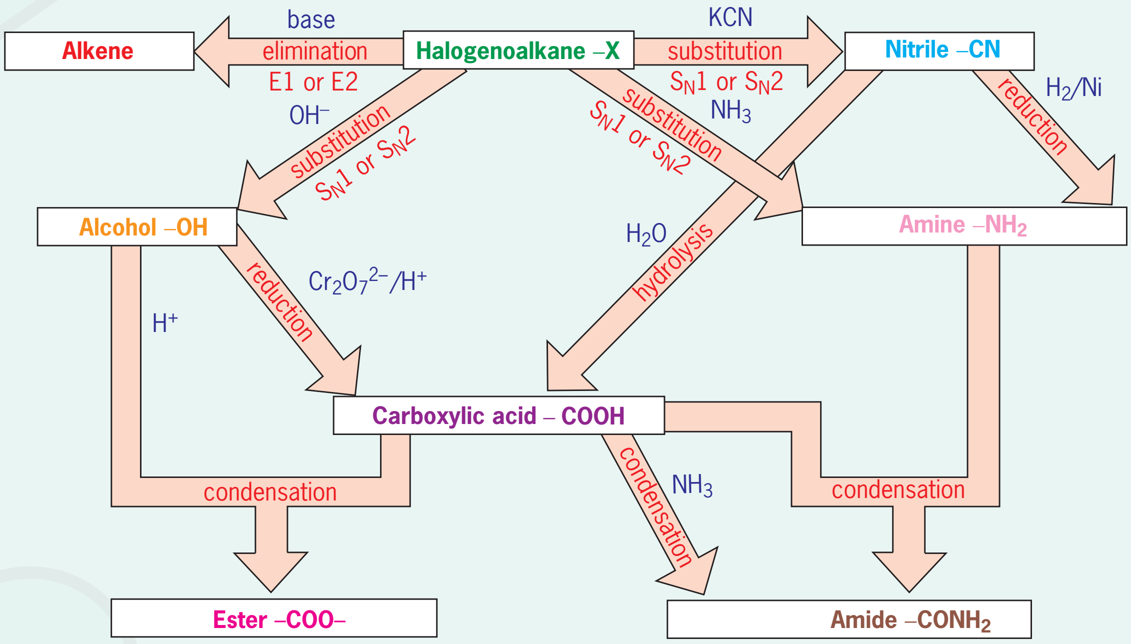
  $RX \rightarrow RCN \rightarrow RCH_2NH_2$

- Isomers are molecules with the same chemical formula but different structural formulas. The types of isomerism are summarized in the flowchart on the next page (bottom).
- Geometric isomers differ in their physical and chemical properties, sometimes marginally, but often significantly. Several steric hindrance and inductive effects may be involved.
- Optical isomers (enantiomers) are said to be chiral. To predict whether a molecule is chiral look for a plane of symmetry. A molecule with such a plane of symmetry cannot be chiral. Chiral molecules contain an asymmetric carbon atom, sometimes indicated by an asterisk. A carbon atom bonded to four different substituents will be chiral.
- Optical isomers differ only in one physical property, the direction of rotation of plane-polarized light. They differ only in one chemical property, their interaction with other optically active compounds.
- In many biological systems one enantiomer is found almost exclusively.

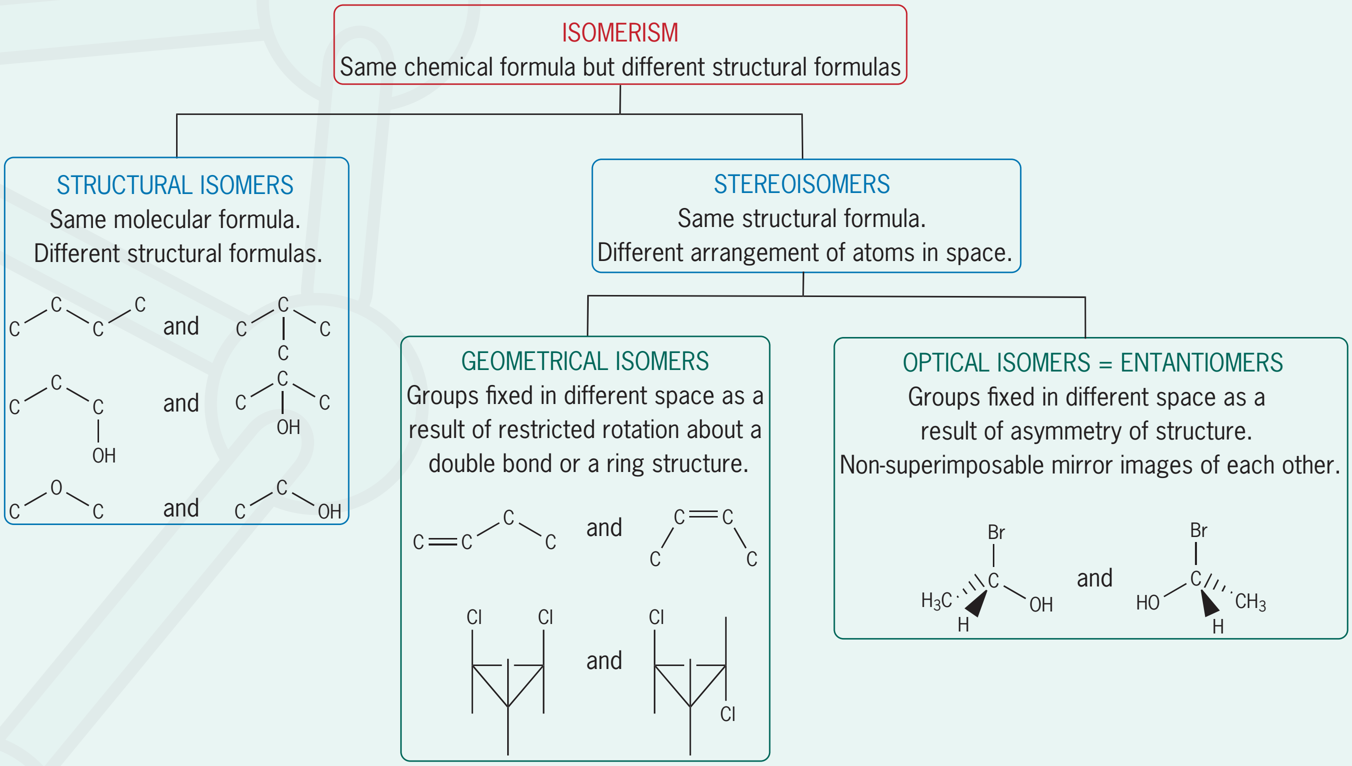
Factor	**Effect on S_N2 reaction rate**	**Effect on S_N1 reaction rate**
Nucleophile	Charged species are stronger nucleophiles than neutral species, e.g. HO^- is a stronger nucleophile than H_2O. Stronger bases are stronger nucleophiles, e.g. NH_3 is a stronger nucleophile than H_2O.	No effect. The nucleophile does not influence step 1, the rate-determining heterolytic fission step.
Halogen leaving group	The weaker the C–X bond the stronger the leaving group, e.g. the weaker C–I bond means that CH_3I is more reactive than CH_3Cl, which contains the stronger C–Cl bond. The order of reactivity for halogenoalkanes is C–I > C–Br > C–Cl.	As for S_N2. The C–X bond strength influences the ease of step 1, the rate-determining heterolytic fission step.
Substrate	Steric hindrance by alkyl groups attached to the C–X carbon atom influences ease of reaction. Primary halogenoalkanes show the least steric hindrance and so react faster than tertiary halogenoalkanes.	Positive inductive effects by alkyl groups attached to the C–X carbon stabilize the carbocation and so influence ease of reaction. Tertiary halogenoalkanes show the greatest inductive or stabilizing effect and so react faster than primary halogenoalkanes.

Halogenoalkane	**S_N1**	**S_N2**	**E1**	**E2**
Primary RCH_2X	Does not occur	Most favoured	Does not occur	Can occur when strong bases (e.g. RO^-) are used
Secondary R_2CHX	Can occur	Occurs in competition with E2	Can occur	Favoured when strong bases (e.g. RO^-) are used
Tertiary R_3CX	Occurs in competition with E1	Does not occur	Occurs in competition with S_N1	Favoured when strong bases (e.g. RO^-) are used

Reaction pathways



Types of isomerism



ISOMERISM
Same chemical formula but different structural formulas

STRUCTURAL ISOMERS
Same molecular formula.
Different structural formulas.

STEREOISOMERS
Same structural formula.
Different arrangement of atoms in space.

GEOMETRICAL ISOMERS
Groups fixed in different space as a result of restricted rotation about a double bond or a ring structure.

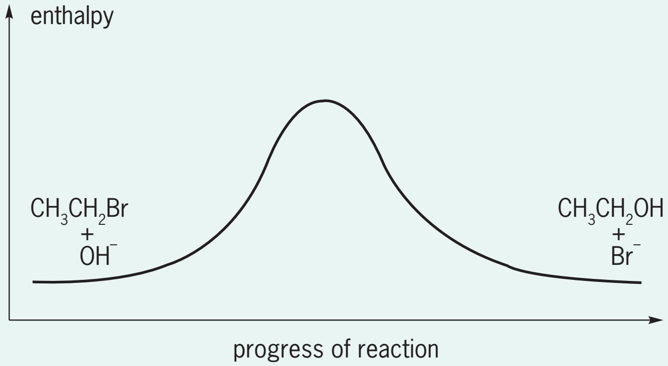
OPTICAL ISOMERS = ENTANTIOMERS
Groups fixed in different space as a result of asymmetry of structure.
Non-superimposable mirror images of each other.

Chapter 9 Review questions

1 Draw structural formulas for a compound of molecular formula $C_5H_{11}NO$ that contains:
   - **a** an aldehyde and a secondary amine
   - **b** a ketone and a primary amine
   - **c** an amide.

2 Draw and name an isomer of:
   - **a** ethanoic acid
   - **b** propanamide
   - **c** 2,2-dimethylpropanenitrile
   - **d** 2-amino-2-methylbutane.

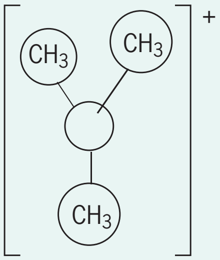
3 The graph below shows the energy profile for a nucleophilic substitution reaction.



   - **a** Identify the reaction as S_N1 or S_N2.
   - **b** Draw a structural diagram of the transition state labelled as X on the diagram.

4 State the type of substitution reaction, S_N1 or S_N2, expected for each of the following reactions.
   - **a** 2-Bromo-2-methylpropane reacts with aqueous sodium hydroxide to form 2-methylpropan-2-ol.
   - **b** Chloromethane reacts with aqueous sodium cyanide to form ethanenitrile.

5 The diagram below shows an intermediate formed in a nucleophilic substitution reaction with the OH^- ion as the nucleophile and the bromide ion as the leaving group.



   - **a** Identify the reaction as S_N1 or S_N2.
   - **b** Draw a diagram to represent the complete reaction mechanism.

6 2-Bromobutane can be converted into butan-2-ol by a nucleophilic substitution reaction. This reaction occurs by two different mechanisms.
   - **a** Draw the structure of the transition state formed in the S_N2 reaction.
   - **b** Draw the structure of the intermediate carbocation formed in the S_N1 reaction.
   - **c** Explain why the rate of the S_N1 reaction will decrease if 2-chlorobutane is used instead of 2-bromobutane.
   - **d** State whether the rate of the S_N2 reaction will increase or decrease if 2-chlorobutane is used instead of 2-bromobutane.

7 **a** State and explain which of the following compounds you would expect to react most rapidly by an S_N1 mechanism.
   - **I** $(CH_3)_3CBr$
   - **II** $CH_3CH_2CH_2CH_2Br$
   - **III** $(CH_3)_3CCl$
   - **IV** $CH_3CH_2CH_2CH_2Cl$

   b State and explain which of the following compounds you would expect to react most rapidly by an S_N2 mechanism.
   - **I** $(CH_3)_3CBr$
   - **II** $CH_3CH_2CH_2CH_2I$
   - **III** $(CH_3)_3CI$
   - **IV** $CH_3CH_2CH_2CH_2Br$

8 The conversion of $(CH_3)_3CI$ to $(CH_3)_3OH$ involves nucleophilic substitution by an S_N1 mechanism.
   - **a** Identify the species responsible for the nucleophilic attack.
   - **b** Explain how the rate of the S_N1 reaction for each of the following with the same nucleophile compares with that of $(CH_3)_3CI$.
     - **i** $(CH_3)_3CBr$
     - **ii** $(CH_3)_2CHI$

9 Pentene, C_5H_{10}, exists in a number of isomeric forms.
   - **a** **i** Draw and name two geometric isomers of pent-2-ene.
     - **ii** Explain why these geometric isomers occur.
   - **b** Pent-2-ene can be converted to 2-bromopentane by an addition reaction.

     Draw the structure of 2-bromopentane and explain why it shows optical isomerism.

c Pent-2-ene can also be converted to 3-bromopentane, which can be converted to 3-pentanol in a nucleophilic substitution by an S_N1 mechanism.

  i Identify the species responsible for the nucleophilic attack.

  ii Explain why the reaction would be likely to occur by an S_N1 mechanism, rather than an S_N2 mechanism.

10 **a** Draw the structural formula of the product obtained from each combination.

  i $CH_3COOH + CH_3CH_2OH$

  ii $CH_3COOH + (CH_3)_2NH$

b Draw structural formulas for the organic reactants used to prepare the following compounds.

  i Ethyl propanoate

  ii *N*-Methylpentanamide

11 Kodol is a copolymer used to make fibres of stain-resistant carpet. The structure of a segment of Kodol is shown (bottom of page).

a Suggest what is meant by the term *copolymer*.

b Draw structural formulas for the monomers used to produce Kodol.

c Was Kodol produced by addition or condensation polymerization? Explain your choice.

12 Polyethene and proteins are both examples of polymers. Explain why proteins are more complex polymers than polyethene.

13 Draw possible two-step reaction pathways for the synthesis of the following compounds from the given starting compounds. Include any inorganic reagents and conditions needed for the pathway.

a Ethanamide from ethanol

b 1-Propylamine from 1-bromoethane

c Diethylamine from ethanol

d Ethyl ethanoate from ethanol

14 Identify which of the following compounds can exist as optical isomers. Explain your choice.

I $CH_3CHBrCH_3$

II $BrCH_2CHBrCH_3$

III $BrCH_2CHBrCH_2Br$

IV $Br_2CHCHBrCHBr_2$

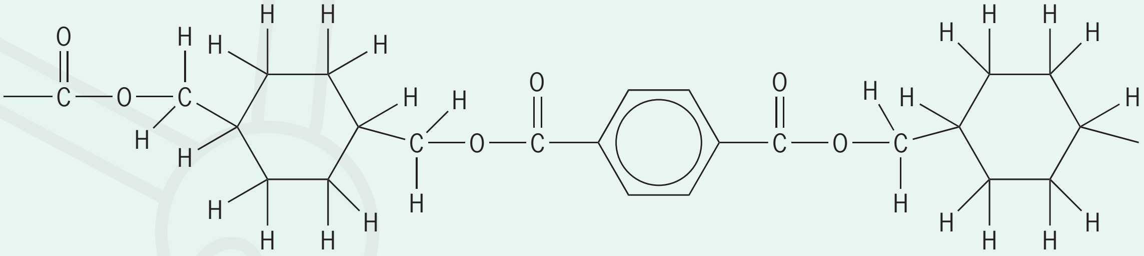
15 For the molecular formula $C_5H_{10}O$, draw structural formulas for:

a two functional group isomers

b a pair of enantiomers

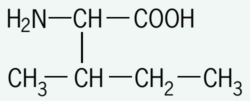
c a pair of non-cyclic *cis–trans* isomers.

16 Explain why the amino acid alanine exists as enantiomers, and describe how pure samples of the enantiomers can be distinguished experimentally.



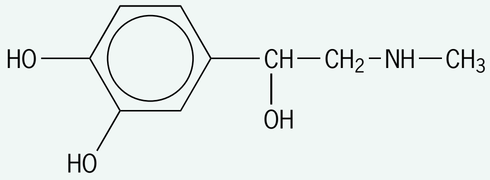
Kodol

17 The amino acid isoleucine is shown below. Copy the structure and label with an asterisk any chiral carbons in the amino acid molecule.



$$\begin{array}{l} H_2N-CH-COOH \\ \qquad\;\; | \\ CH_3-CH-CH_2-CH_3 \end{array}$$

18 Many drugs consist of optically active molecules whose activity depends on the particular enantiomer used. Adrenaline is one such optically active molecule.



a Circle the hydroxyl group in the adrenaline molecule shown above.

b Identify the amino functional group in adrenaline as primary, secondary or tertiary.

c Identify by means of an asterisk (*) the asymmetric carbon atom in the adrenaline molecule.

19 Consider the four structural isomers of C_4H_9Br.

a One of these isomers, $CH_3CHBrCH_2CH_3$ is optically active.

State the name of this isomer and explain why it is optically active.

b Draw and name the other three structural isomers.

c Identify one isomer in part **b** that undergoes a substitution reaction mainly by an S_N2 mechanism.

d Write the S_N2 mechanism for the reaction that occurs when the isomer identified in part **c** is warmed with aqueous sodium cyanide.

20 The compound 2-bromobutane, $CH_3CHBrCH_2CH_3$, can react with sodium hydroxide to form three different compounds.

a **i** Name the product that contains an oxygen atom.

ii Name the type of reaction which produces the product given in part **i**.

b The two other products, C_4H_8, are structural isomers.

i Draw diagrams to shows the relationship between these two isomers.

ii One of these structural isomers exists as a pair of geometric isomers. Draw and name these geometric isomers.

c Draw a mechanism diagram to show formation of C_4H_8 from $CH_3CHBrCH_2CH_3$.

Web Destinations www.pearsoned.com.au/schools

Weblinks are available on the Companion Website to support learning and research related to this chapter.

Chapter 9 Test

Part A: Multiple-choice questions

1 Which molecule possesses a chiral centre?

A NH_2CH_2COOH

B $CH_3CH(NH_2)COOH$

C $CH_3C(NH_2)_2COOH$

D $(CH_3)_2C(NH_2)COOH$

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2 Nylon is a condensation polymer made up of hexanedioic acid and 1, 6-diaminohexane. Which type of linkage is present in nylon?

A Amide

B Ester

C Amine

D Carboxyl

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3 Which pair of compounds can be used to prepare CH_3COOCH_3?

A Ethanol and methanoic acid

B Methanol and ethanoic acid

C Ethanol and ethanoic acid

D Methanol and methanoic acid

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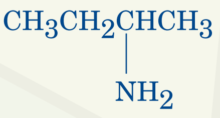
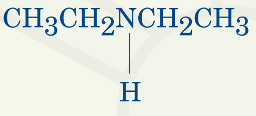
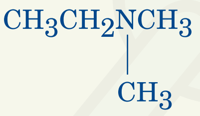
4 Which one of the following compounds is optically active?

A $CH_3CH_2CH_2CH_2NH_2$

B

$CH_3CH_2\underset{\underset{NH_2}{|}}{C}HCH_3$

C

$CH_3CH_2\underset{\underset{H}{|}}{N}CH_2CH_3$

D

$CH_3CH_2\underset{\underset{CH_3}{|}}{N}CH_3$

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For more multiple-choice test questions, connect to the Companion Website and select Review Questions for this chapter.

5 Consider the following reaction:

$CH_3COOH + NH_3 \rightarrow CH_3COONH_4 \rightarrow CH_3CONH_2$

What will be the final product if aminoethane (ethylamine) is used instead of NH_3?

A $CH_3CONHCH_2CH_3$

B $CH_3CONHCH_3$

C CH_3CONH_2

D $CH_3CONH_2CH_2CH_3$

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6 The alkaline hydrolysis of primary halogenoalkanes usually follows an S_N2 mechanism. For which compound would the rate of hydrolysis be fastest?

A $CH_3CH_2CH_2F$

B $CH_3CH_2CH_2Cl$

C $CH_3CH_2CH_2Br$

D $CH_3CH_2CH_2I$

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7 Which of the following is an amine?

A $CH_3CH_2NH_2$

B CH_3CONH_2

C $-[CH_2CONHCH_2CO]_n-$

D $CH_3CH_2C{\equiv}N$

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8 $CH_3OH + CH_3CH_2COOH \overset{H^+}{\rightleftharpoons} CH_3CH_2COOCH_3 + H_2O$

The forward reaction represented by the equation above is:

A an addition

B an esterification

C a hydrolysis

D an oxidation

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9 Which substance is most likely to react with hydroxide ions by means of an S_N1 mechanism?

A C_6H_5Cl

B $(CH_3)_3CCl$

C $(CH_3)_2CHCH_2Cl$

D $CH_3CH_2CH_2CH_2Cl$

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10 Which compound reacts fastest with water?

A $(CH_3)_3CBr$

B $(CH_3)_3CCl$

C $CH_3CH_2CH_2CH_2Br$

D $CH_3CH_2CH_2CH_2Cl$

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(10 marks)

Part B: Short-answer questions

1 **a** There are **geometrical** isomers of the cyclic compound $C_4H_6Cl_2$. Draw the structural formula of two isomers and explain why these two isomers exist.

i *cis*-isomer

ii *trans*-isomer

(3 marks)

b **i** Draw the structural formulas of **two** isomers of but-2-ene-1,4-dioic acid.

(2 marks)

ii State and explain which isomer will have a lower melting point.

(2 marks)

iii Describe how the two isomers can be distinguished by a chemical test.

(2 marks)

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2 Compounds of formula C_4H_7Cl exhibit both geometrical and optical isomerism.

a Explain why C_4H_7Cl shows geometrical isomerism.

(1 mark)

b Draw the *cis* and *trans* isomers of C_4H_7Cl.

(2 marks)

c Draw the structural formula of C_4H_7Cl that shows only optical isomerism. Show the chiral carbon atom with an *.

(2 marks)

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3 Explain why butan-2-ol, $CH_3CH(OH)CH_2CH_3$, exists as *enantiomers*, and describe how pure samples of the enantiomers can be distinguished experimentally.

(3 marks)

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4 Ethanal can be used as the starting material for the preparation of an ester. The steps can be summarized as follows:

$$CH_3CHO \xrightarrow{\text{step 1}} CH_3COOH$$
$$\xrightarrow{\text{step 2}} CH_3COOCH_2CH_3$$

a State the name of the other organic compound needed for step 2.

(1 mark)

b State the name of the ester formed.

(1 mark)

© IBO SL Paper 2 Nov 06 Q5d (part of)

Part C: Data-based questions

1 2-bromobutane can be converted into butan-2-ol by a nucleophilic substitution reaction. This reaction occurs by two different mechanisms.

a Give the structure of the transition state formed in the S_N2 mechanism.

(2 marks)

b Write the equations for the S_N1 mechanism.

(2 marks)

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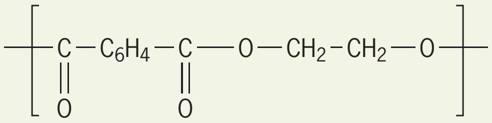
2 **a** Polyesters are formed in a condensation reaction. The structure of the repeat unit of a polyester is



$$\left[\underset{\underset{\textstyle O}{\|}}{C} - C_6H_4 - \underset{\underset{\textstyle O}{\|}}{C} - O - CH_2 - CH_2 - O \right]$$

i Draw the structures of the two monomers that react to form this polyester.

(2 marks)

ii Identify the essential feature of the monomers in part **i** that enable them to form a condensation polymer.

(1 mark)

b **i** Name the following compounds or identify the functional groups in the following organic molecules.

I H_2CO

II $HOOC–C_2H_4–COOH$

III C_2H_4

IV $H_2N–C_2H_4–NH_2$

(2 marks)

ii Which two of the four compounds in part **b** will form a condensation polymer? Draw the simplest repeating unit for the polymer.

(2 marks)

iii One of the four compounds undergoes addition polymerization. Write a balanced chemical equation for this reaction, showing the structure of the repeating unit of the product.

(1 mark)

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Part D: Extended-response question

The rates and mechanisms of nucleophilic substitution reactions depend on several factors.

a Both CH_3Br and $(CH_3)_3CBr$ react with aqueous sodium hydroxide. Identify the type of nucleophilic substitution in each reaction. Explain each mechanism in terms of the inductive and steric effects.

(6 marks)

b State and explain the relative rates of reaction of CH_3Br with OH^- and H_2O.

(3 marks)

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Total marks: 50

APPENDIX 1

Table of relative atomic masses

Element	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	(227)
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	(210)
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	(251)
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.55
Curium	Cm	96	(247)
Darmstadtium	Ds	110	(271)
Dubnium	Db	105	(262)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(254)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.59
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(277)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.01
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.22
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(260)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	(268)
Mendelevium	Md	101	(258)
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	(259)
Osmium	Os	76	190.21
Oxygen	O	8	16.00
Palladium	Pd	46	106.42
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	(210)
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	146.92
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.21
Rhodium	Rh	45	102.91
Roentgenium	Rg	111	(272)
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	98.91
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

Note: Numbers shown in brackets indicate the relative isotopic mass of the most stable isotope when the atomic mass is not known.

APPENDIX 2

Physical constants and some useful equations

Physical constants

Name of constant	Symbol	Value
Absolute zero	0 K	–273°C
Avogadro’s constant	L	6.02×10^{23} mol^{-1}
Gas constant	R	8.31 J K^{-1} mol^{-1}
Molar volume of a gas at 273 K and 1.01×10^{5} Pa	V_m	22.4 dm^{3} mol^{-1}
Planck’s constant	h	6.63×10^{-34} J s
Specific heat capacity of water	c	4.18 J g^{-1} K^{-1} (4.18 kJ kg^{-1} K^{-1})
Ionic product constant for water	K_w	1.00×10^{-14} mol^{2} dm^{-6} at 298 K
1 atm		1.01×10^{5} Pa
1 dm^{3} = 1 litre		1×10^{-3} m^{3} = 1×10^{3} cm^{3}

Some useful equations

$$E = hf$$

$$PV = nRT$$

$$G^{\ominus} = H^{\ominus} - TS^{\ominus}$$

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln k = \frac{-E_a}{RT} + \ln A$$

$$\mathrm{pH} = \mathrm{p}K_a = \log \frac{[\mathrm{salt}]}{[\mathrm{acid}]}$$

A review of formulas required for molar calculations

Formula	Quantities	Used when …
$n = \frac{m}{M}$	n = amount (mol) m = mass (g) M = molar mass (g mol^{-1})	masses (usually of solids or liquids) are given or required
$n = \frac{N}{L}$	n = amount (mol) N = number of particles L = Avogadro’s constant (6.02×10^{23} mol^{-1})	numbers of atoms, ions or molecules are given or required
$n = cV$	n = amount (mol) c = concentration (mol dm^{-3}) V = volume of solution (dm^{3})	volumes or concentrations of solutions are given or required
$n = \frac{V}{V_m}$	n = amount (mol) V = volume of gas (dm^{3}) V_m = molar volume (dm^{3} mol^{-1})	volumes of gases are given or required at STP
$n = \frac{PV}{RT}$	n = amount (mol) P = pressure (kPa) V = volume of gas (dm^{3}) R = gas constant (8.31 J K^{-1} mol^{-1}) T = temperature (K)	Volumes and pressures of gases are given or required at any temperature

APPENDIX 3

Thermochemical data for a selection of compounds and elements

Substance	**Formula**	**State**	$H_f^\ominus$ **(kJ mol^{-1})**	$G_f^\ominus$ **(kJ mol^{-1})**	$S^\ominus$ **(J K^{-1} mol^{-1})**
Methane	CH_4	g	–75	–51	186
Ethane	C_2H_6	g	–85	–33	230
Propane	C_3H_8	g	–104	–24	270
Butane	C_4H_{10}	g	–125	–16	310
Pentane	C_5H_{12}	l	–173	–9	261
Hexane	C_6H_{14}	l	–199	–4	296
Ethene	C_2H_4	g	+52	68	219
Propene	C_3H_6	g	+20	63	267
But-1-ene	C_4H_8	g	+1	72	307
Ethyne	C_2H_2	g	+227	209	201
Methanol	CH_3OH	g	–201	–162	238
Methanol	CH_3OH	l	–239	–166	127
Ethanol	C_2H_5OH	g	–235	–169	282
Ethanol	C_2H_5OH	l	–278	–175	161
Chloroethane	C_2H_5Cl	g	–105	–53	276
Ethylamine	$C_2H_5NH_2$	g	–49	37	285
Benzene	C_6H_6	g	83	130	269
Benzene	C_6H_6	l	49	125	173
Methanoic acid	$HCOOH$	l	–409	–346	129
Ethanoic acid	CH_3COOH	l	–487	–392	160
Carbon dioxide	CO_2	g	–394	–394	214
Water	H_2O	g	–242	–229	189
Water	H_2O	l	–286	–237	70
Ammonia	NH_3	g	–46	–17	193
Ammonium chloride	NH_4Cl	s	–314	–204	95
Nitrogen monoxide	NO	g	90	87	211
Nitrogen dioxide	NO_2	g	34	52	240
Dinitrogen tetroxide	N_2O_4	g	10	98	304
Hydrogen bromide	HBr	g	–36	–53	199
Hydrogen chloride	HCl	g	–92	–95	187
Oxygen	O_2	g	0	0	205
Ozone	O_3	g	142	163	238
Hydrogen	H_2	g	0	0	131
Nitrogen	N_2	g	0	0	192
Chlorine	Cl_2	g	0	0	223
Sulfur dioxide	SO_2	g	–297	–300	249
Sulfur trioxide	SO_3	g	–396	–371	256

APPENDIX 4

Lattice enthalpies at 298 K

TABLE A4.1 EXPERIMENTAL LATTICE ENTHALPIES FOR SOME IONIC COMPOUNDS

Substance	$H^{\ominus}_{\text{lattice}}$ (kJ mol^{-1})	Substance	$H^{\ominus}_{\text{lattice}}$ (kJ mol^{-1})
LiF	1022	CaF_2	2602
LiCl	846	$BeCl_2$	3006
LiBr	800	$MgCl_2$	2493
LiI	744	$CaCl_2$	2237
NaF	902	$SrCl_2$	2112
NaCl	771	$BaCl_2$	2018
NaBr	733	MgO	3889
NaI	684	CaO	3513
KF	801	SrO	3310
KCl	701	BaO	3152
KBr	670	MgS	3238
KI	629	CaS	2966
RbF	767	SrS	2779
RbCl	675	BaS	2643
RbBr	647	CuCl	976
RbI	609	AgF	955
CsF	716	AgCl	905
CsCl	645	AgBr	890
CsBr	619	AgI	876
CsI	585	NH_4Cl	640

TABLE A4.2 THEORETICAL LATTICE ENTHALPIES FOR SOME IONIC COMPOUNDS

Substance	$H^{\ominus}_{\text{lattice}}$ (kJ mol^{-1})	Substance	$H^{\ominus}_{\text{lattice}}$ (kJ mol^{-1})
LiF	1004	CsF	728
LiCl	833	CsCl	636
LiBr	787	CsBr	611
LiI	728	CsI	582
NaF	891	CaF_2	2611
NaCl	766	MgO	3929
NaBr	732	CaO	3477
NaI	686	SrO	3205
KF	795	BaO	3042
KCl	690	AgF	870
KBr	665	AgCl	770
KI	632	AgBr	758
RbF	761	AgI	736
RbCl	674		
RbBr	644		
RbI	607		

APPENDIX 5

TABLE A5.1 K_a VALUES AT 25°C FOR SOME COMMON WEAK ACIDS

Name	Formula	pK_a	K_a value (mol dm^{-3})
Methanoic acid	$HCOOH$	3.74	1.82×10^{-4}
Ethanoic acid	CH_3COOH	4.76	1.74×10^{-5}
Propanoic acid	CH_3CH_2COOH	4.87	1.35×10^{-5}
Butanoic acid	$CH_3CH_2CH_2COOH$	4.82	1.51×10^{-5}
Pentanoic acid	$CH_3(CH_2)_3COOH$	4.86	1.38×10^{-5}
Benzoic acid	C_6H_5COOH	4.20	6.31×10^{-5}
Phenylethanoic acid	$C_6H_5CH_2COOH$	4.31	4.90×10^{-5}
Chloroethanoic acid	$CH_2ClCOOH$	2.86	1.38×10^{-3}
Dichloroethanoic acid	$CHCl_2COOH$	1.29	5.13×10^{-2}
Trichloroethanoic acid	CCl_3COOH	0.65	2.24×10^{-1}
Phenol	C_6H_5OH	10.00	1.00×10^{-10}
Ethanol	C_2H_5OH	16.0	1.00×10^{-16}
Boric acid	H_3BO_3	9.24	5.75×10^{-10}
Hypochlorous acid	$HOCl$	7.54	2.88×10^{-8}
Hydrocyanic acid	HCN	9.22	6.03×10^{-10}
Hydrofluoric acid	HF	3.17	6.76×10^{-4}
Nitrous acid	HNO_2	3.14	7.24×10^{-4}

TABLE A5.2 K_b VALUES AT 25°C FOR SOME COMMON WEAK BASES

Name	Formula	pK_b	K_b value (mol dm^{-3})
Ammonia	NH_3	4.75	1.8×10^{-5}
Methylamine	CH_3NH_2	3.36	4.4×10^{-4}
Ethylamine	$CH_3CH_2NH_2$	3.27	6.4×10^{-4}
Dimethylamine	$(CH_3)_2NH$	3.28	5.4×10^{-4}
Trimethylamine	$(CH_3)_3N$	4.20	6.3×10^{-5}
Diethylamine	$(CH_3CH_2)_2NH$	3.07	8.51×10^{-4}
Triethylamine	$(CH_3CH_2)_3N$	3.36	4.37×10^{-4}
Phenylamine	$C_6H_5NH_2$	9.38	4.5×10^{-10}
Pyridine	C_5H_5N	8.77	1.7×10^{-9}
Hydrazine	H_2NNH_2	5.89	1.3×10^{-6}

TABLE A5.3 pK_a VALUES AND pH OF COLOUR CHANGE FOR SOME ACID–BASE INDICATORS

Indicator	Colour of acidic form	pK_a (pK_{in})	pH range of colour change	Colour of basic form
Methyl orange	Red	3.7	3.1–4.4	Yellow
Bromophenol blue	Yellow	4.0	3.0–4.6	Blue
Bromocresol green	Yellow	4.7	3.8–5.4	Blue
Methyl red	Red	5.1	4.4–6.2	Yellow
Bromothymol blue	Yellow	7.0	6.0–7.6	Blue
Phenol red	Yellow	7.9	6.8–8.4	Red
Phenolphthalein	Colourless	9.3	8.3–10.0	Pink-purple

APPENDIX 6

Standard electrode potentials

Oxidized species	$\rightleftharpoons$	Reduced species	$E^\ominus$ volts
$Li^+(aq) + e^-$	$\rightleftharpoons$	$Li(s)$	–3.03
$K^+(aq) + e^-$	$\rightleftharpoons$	$K(s)$	–2.92
$Ca^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ca(s)$	–2.87
$Na^+(aq) + e^-$	$\rightleftharpoons$	$Na(s)$	–2.71
$Mg^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mg(s)$	–2.36
$Al^{3+}(aq) + 3e^-$	$\rightleftharpoons$	$Al(s)$	–1.66
$Mn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Mn(s)$	–1.18
$H_2O(l) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g) + OH^-(aq)$	–0.83
$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76
$Fe^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Fe(s)$	–0.44
$Ni^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Ni(s)$	–0.23
$Sn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Sn(s)$	–0.14
$Pb^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Pb(s)$	–0.13
$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
$Cu^{2+}(aq) + e^-$	$\rightleftharpoons$	$Cu^+(aq)$	+0.15
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2SO_3(aq) + H_2O(l)$	+0.17
$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
$\frac{1}{2}O_2(g) + H_2O(l) + 2e^-$	$\rightleftharpoons$	$2OH^-(aq)$	+0.40
$Cu^+(aq) + e^-$	$\rightleftharpoons$	$Cu(s)$	+0.52
$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	$I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^-$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80
$\frac{1}{2}Br_2(l) + e^-$	$\rightleftharpoons$	$Br^-(aq)$	+1.09
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$	$\rightleftharpoons$	$H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\rightleftharpoons$	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$\frac{1}{2}F_2(g) + e^-$	$\rightleftharpoons$	$F^-(aq)$	+2.87

SOLUTIONS

These solutions have been simplified. Fully explained answers, including fully worked solutions to calculations and answers requiring a diagram, may be found on the *Chemistry: For use with the IB Diploma Programme Higher Level* student CD packaged with this book.

Chapter 1 Atomic structure

Section 1.1

1 Successive ionization energies are the energies required to remove all the electrons from one mole of atoms of an element in the gaseous state, one mole of electrons at a time.

2 The second ionization energy for lithium (7298 kJ mol^{-1}) is significantly greater than the first (513.3 kJ mol^{-1}).

3 **a** group 5
b No, as only the first six ionization energies have been given.

4 **a** Na is in group 1, Al is in group 3, S is in group 6.
b sodium

5 magnesium

Section 1.2

2 They are both spherical; however, the radius of a 2s orbital is greater than that of a 1s orbital.

4 **a** They are at right angles.
b They are at right angles.

5 **a** > 3s subshell **b** >> 2p subshell **c** < 3d subshell

6 1s < 2p < 3p < 4s < 3d

7 **a** 9
b 3s (1 orbital), 3p (3 orbitals) and 3d (5 orbitals)

8 **a** 16 **b** 4f subshell

Section 1.3

1 **a** 2 **b** 2 **c** 10 **d** 8 **e** 2

3 There is one in p_x, one in p_y and one in p_z.

4 **a** s-block **b** p-block **c** d-block
d p-block **e** f-block **f** d-block

5 **a** 2p **b** 3d **c** 5s
d 3p **e** 4p **f** 4d

6 **a** $1s^2\ 2s^2\ 2p^3$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8\ 4s^2$
e $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$
f $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^2$

7 **a** $1s^2\ 2s^2\ 2p^6$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

8 **a** $1s^2\ 2s^2\ 2p^6$
b $1s^2\ 2s^2\ 2p^6$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$

Chapter 1 Review questions

1 It is the amount of energy required to remove one mole of electrons from one mole of an element in the gaseous state.

4 The first six successive ionization energies of sulfur would increase gradually, then the seventh would be significantly larger than the sixth.

5 beryllium

7 **a** **i** spherical
ii 'dumbbell' shaped
b **i** It is centred at the point where the axes cross.
ii It is aligned along the *y*-axis of a set of 3-dimensional axes with one lobe on the positive side of the axis and the other lobe along the negative side.

9 4p > 3d > 4s > 3p > 2s

10 Only 8 electrons can exist in the second energy level, so there are none available for a 2d orbital.

11 16 orbitals

12 They have the same shape, same dimensions, but different alignment.

13 **a** 12 **b** 10 **c** 7

16 **a** **i** Li: 2s **ii** 1
b **i** F: 2p **ii** 5
c **i** Pd: 4d **ii** 8
d **i** Ba: 6s **ii** 2
e **i** Xe: 5p **ii** 6
f **i** Ge: 4p **ii** 2

17 **a** $1s^2\ 2s^2$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4\ 3d^2$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$
d $1s^2\ 2s^2\ 2p^6\ 3s^1$
e $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^3\ 5s^2$
f $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

18 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
c $1s^2\ 2s^2\ 2p^6$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

19 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
d $1s^2$

20 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^1$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^5\ 5s^1$

Chapter 1 Test

Part A: Multiple-choice questions

1 D **2** C **3** D **4** C **5** B
6 D **7** C **8** C **9** B **10** C

Chapter 2 Bonding

Section 2.1

2 A negative charge centre is a pair, or multiple pairs of bonding or non-bonding electrons around a central atom.

5 The repulsion between a non-bonding pair of electrons and a bonding pair of electrons is greater than the repulsion between two bonding pairs of electrons.

6 The repulsion between a non-bonding pair of electrons and a bonding pair of electrons is less than the repulsion between two non-bonding pairs of electrons.

Section 2.2

3 **a** σ bond **b** π bond
c **i, ii** σ bond

5 **a** sp^2 hybridization **b** sp hybridization
c sp^3 hybridization

6 **a** 2 sp^3 hybridized orbitals overlap in a σ bond.
b 2 sp^3 hybridized orbitals overlap in a σ bond and the sideways overlapping of 2 unhybridized p orbitals forms a π bond.
c 2 sp hybridized orbitals overlap in a σ bond and 2 pairs of unhybridized p orbitals overlap sideways forming two π bonds.

8 The nitrogen atom in ammonia has sp^3 hybridization.

Section 2.3

1 The experimentally determined arrangement of atoms was not adequately described by a single Lewis structure.

3 All equal and shorter than a sulfur–oxygen single bond but longer than a sulfur–oxygen double bond.

4 **a** benzene, C_6H_6; ozone, O_3; naphalene, $C_{10}H_8$
b p orbials

5 **a** SO_3^{2-} and O_3

8 **a** The π bond in CH_3COO^- is delocalized.
b The π bond in CH_3COOH is localized.

Chapter 2 Review questions

3 **a** **i** three **ii** trigonal planar
b **i** two or five **ii** linear
c **i** four **ii** tetrahedral
d six or five; if six, then square planar or octahedral, if five then trigonal bipyramidal

5 **a** 120° **b** 180° **c** 90° **d** 90°

8 **a** Orbital overlap is a shared region of space between two atoms.
b The shared region of space (orbital overlap) can be occupied by two electrons (with opposite spin) which form a covalent bond.

9

Bond angle	Hybridization of orbitals	Shape (name only)
120°	sp^2	Trigonal planar
180°	sp	Linear
109.5°	sp^3	Tetrahedral

10 **a** sp^2 **b** sp^3 **c** sp

11 **a** sp: carbon atom number 1
b sp^2: carbon atoms numbered 4, 5, and 7
c sp^3: carbon atoms numbered 2, 3, and 6

12 See chapter 2, figures 2.2.23 (N_2) and 2.2.10 (N_2H_4).

13 **a** The carbon atom has sp hybridization.
b The carbon atom has sp^2 hybridization.
c The nitrogen atom has sp^3 hybridization.

14 **a** **ii** Carbons 1 and 2 are sp^2 hybridized; carbon 3 is sp^3 hybridized.
iii σ bonds occur between all pairs of carbon atoms; in addition, π bonds occur between carbons 1 and 2.
b **ii** The CH_3 carbon is sp^3 hybridized and carbons 1–6 in the ring are sp^2 hybridized.
iii σ bonds occur between all pairs of carbon atoms; in addition π bonds occur between carbons 2 to 7.
c **ii** Carbons 1, 4 and 5 are sp^3 hybridized and carbons 2 and 3 are sp^2 hybridized.
iii σ bonds occur between all pairs of carbon atoms; in addition π bonds occur between carbons 2 and 3.

16 There will be 6 π bonds in squalene.

17 In H_2SO_4 the S–O bonds are fixed as being single (bonded to a hydrogen atom) or double, so resonance structures are not possible. The bond lengths would also be different; S–O would be longer than S=O. In SO_4^{2-} ions all bonds are equal.

18 The resonance structures have alternating double and single bonds, whereas the structure with a ring shows the delocalization of the 6 π electrons.

19 **a** 6 **b** 2 **c** 6 **d** 4

20 They both can explain the equal lengths of the C–O bonds.

Chapter 2 Test

Part A: Multiple-choice questions

1 B **2** B **3** B **4** C **5** A
6 B **7** D **8** A **9** B **10** C

Chapter 3 Periodicity

Section 3.1

1 NaCl is ionic lattice; PCl_3 is covalent molecular.

2 $Na_2O(l)$ has ions that are free to move; liquid SO_3 has no moving charged particles.

3 Covalent molecular bonding. There are no charged particles that are free to move.

4 Sodium ions and chloride ions dissociate, are surrounded by water molecules and become part of a solution.

5 A hydrolysis reaction occurs:
$PCl_5(s) + 4H_2O(l) \rightarrow 5HCl(aq) + H_3PO_4(aq)$

7 Aluminium chloride acts as both a Lewis acid and a Brønsted–Lowry acid.
$AlCl_3(s) + 6H_2O \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$
$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$

8 **a** $Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + HCl(aq)$
b $SiCl_4(l) + 2H_2O(l) \rightarrow 4HCl(aq) + SiO_2(s)$
c $MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

Section 3.2

1 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ or $[Ar]3d^3$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ or $[Ar]3d^{10}$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ or $[Ar]3d^3$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ or $[Ar]3d^6$

2 **a** +4 **b** +5 **c** +6
d +7 **e** +3 **f** +2
3 **a** $ScCl_3$ **b** $CoCl_3$ **c** $ZnCl_2$
4 **a** TiO_2 **b** Ni_2O_3 **c** CrO_3
5 **a** $Fe^{2+} \rightarrow Fe^{3+} + e^-$
b $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
c $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$
7 **a** greater surface area
b heterogeneous
c increased conversion to products

Section 3.3

1 A normal covalent bond is made up of two electrons, one from each of two different atoms; a coordinate bond is made up of two electrons, both from the same atom.
3 **a** 3+ **b** 3+ **c** 3+
5 **a** blue **b** +5
c The colour changes occur as the vanadium is reduced.
6 **a** octahedral **b** octahedral **c** tetrahedral
d linear **e** square planar
9 The nature of the ligands affects the degree of splitting of the 3d orbitals and a different energy of light is absorbed.

Chapter 3 Review questions

1

Compound	State	Bonding
$MgCl_2$	Solid	Ionic
SiO_2	Solid	Covalent lattice
Na_2O	Solid	Ionic
Al_2O_3	Solid	Ionic
Cl_2	Gas	Covalent molecular
SO_2	Gas	Covalent molecular

4 **a** **i** ionic layer lattice
ii covalently bonded molecules that form dimers at reduced pressures
iii at high temperatures, trigonal planar molecules
b **i** Ions are present in the structure, but are not free to move.
ii Aluminium chloride dimers are not charged.
5 **a** NaCl(l) has ions present that are free to move, so it conducts electricity well. In comparison, $SiCl_4$(l) has non-polar molecules, so it does not conduct electricity.
b NaCl in water pH = 7; $SiCl_4$ in water pH ≈ 0
6 **a** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$
b $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$
d $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
7 **a** $2Cr^{3+}(aq) + 7H_2O(l) + 6e^- \rightarrow Cr_2O_7^{2-}(aq) + 14H^+(aq)$
b Colour changes from green to orange.
9 Only one ion exists and that ion does not have a partially filled d-subshell.
12 **a** A ligand is a molecule or ion with an electron pair that it can donate to a transition metal ion to form a transition metal complex.
b H_2O, OH^-, NH_3, CN^-, and Cl^-
13 The Cu^{2+} is behaving as a Lewis acid, an electron pair acceptor, and the H_2O is a Lewis base, an electron pair donor.
17 **a** +3
b $[:C{\equiv}N:]^-$
c $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

19

	a	**b**	**c**
Cu	+1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$	e.g. CuO
	+2	$1s^2\ 2s^2\ 2p^6\ 03s^2\ 3p^6\ 3d^9$	e.g. Cu_2O
V	+2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$	e.g. VCl_2
	+3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$	e.g. VO_2^+
Mn	+2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$	e.g. $MnCl_2$
	+7	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	e.g. MnO_4^-

Chapter 3 Test

Part A: Multiple-choice questions

1 A **2** A **3** D **4** A **5** A
6 C **7** B **8** B **9** D **10** B

Chapter 4 Energetics

Section 4.1

1 The conversion of a gas to a liquid is endothermic, so the value will be more negative.
2 $\Delta H_f^\ominus$ is the enthalpy change that results when one mole of a compound is formed from its elements at a pressure of 1.01×10^2 kPa and 298 K.
$C(s) + 2H_2(g) \rightarrow CH_4(g)$
3 By convention, the standard enthalpy change of formation of any element in its most stable form is zero. Graphite is the more stable form of carbon.
4 greater than
5 $\Delta H_{rxn}^\ominus = -198.2\ \text{kJ mol}^{-1}$
6 $\Delta H_c^\ominus = -1257\ \text{kJ mol}^{-1}$
7 $\Delta H_{rxn}^\ominus = -10\ \text{kJ mol}^{-1}$
8 $\Delta H_c^\ominus = -1928\ \text{kJ mol}^{-1}$
9 $\Delta H_f^\ominus(C_3H_7OH(l)) = -140\ \text{kJ mol}^{-1}$
10 $\Delta H_f^\ominus(CH_3CHO(l)) = -105\ \text{kJ mol}^{-1}$

Section 4.2

2 **a** $K(s) \rightarrow K(g)$ **b** $Br_2(g) \rightarrow 2Br(g)$
c $K(g) \rightarrow K^+(g) + e^-$ **d** $Br(g) + e^- \rightarrow Br^-(g)$
e $K(s) + \frac{1}{2}Br_2(l) \rightarrow KBr(s)$ **f** $KBr(s) \rightarrow K^+(g) + Br^-(g)$
3 **a** $Na_2O(s)$
b Enthalpy of atomization, $\Delta H_{at}^\ominus$
c First ionization energy, $\Delta H_I^\ominus$
d First and second electron affinities, $\Delta H_E^\ominus$
e Enthalpy of lattice formation, $\Delta H_{lf}^\ominus$
4 $\Delta H_l^\ominus(RbCl) = +692\ \text{kJ mol}^{-1}$
6 **a** KCl **b** MgO **c** MgO
d LiF **e** $CaCl_2$
7 Each ion is a sphere with its charge uniformly distributed over the surface.
9 KF < CaO < LiI < AgBr

Section 4.3

1 Entropy is the randomness or disorder of a system.

4 II < III < V < I < IV

5 **a** negative **b** positive **c** negative
d positive **e** positive

6 II < IV < I < III

7 $\Delta S^{\ominus} = -119 \text{ J K}^{-1} \text{ mol}^{-1}$

8 **a** $\Delta S^{\ominus} = +75 \text{ J K}^{-1} \text{ mol}^{-1}$ **b** $\Delta S^{\ominus} = +315 \text{ J K}^{-1} \text{ mol}^{-1}$
c $\Delta S^{\ominus} = -120 \text{ J K}^{-1} \text{ mol}^{-1}$ **d** $\Delta S^{\ominus} = -191 \text{ J K}^{-1} \text{ mol}^{-1}$

Section 4.4

1 $\Delta G^{\ominus}$ is the energy available to do useful work.

2 A negative value for $\Delta G^{\ominus}$ accompanies a spontaneous reaction.

3 **a** Positive value of $\Delta G^{\ominus}$.
b Value of $\Delta G^{\ominus}$ is dependent on temperature: It will be negative at high temperatures and positive at low temperatures.
c Value of ΔG° is dependent on temperature. It will be positive at high temperatures and negative at low temperatures.
d Negative value of $\Delta G^{\ominus}$.

4 **a** Reaction A: $\Delta G^{\ominus} = +3.06 \text{ kJ mol}^{-1}$
Reaction B: $\Delta G^{\ominus} = +34.8 \text{ kJ mol}^{-1}$
Neither reaction A nor B is spontaneous at 298 K.
b At 498 K: Reaction A; $\Delta G^{\ominus} = -2.94 \text{ kJ mol}^{-1}$
At 498 K only reaction A is spontaneous.

5 $\Delta G^{\ominus} = -127 \text{ kJ mol}^{-1}$

6 For the reaction $Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$
$\Delta H^{\ominus}_{rxn} = +96 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus}_{rxn} = 138 \text{ J K}^{-1}$
At 250 K, $\Delta G^{\ominus} = 61.5 \text{ kJ mol}^{-1}$.
At 850 K, $\Delta G^{\ominus} = -21.3 \text{ kJ mol}^{-1}$.

7 7320 K

8 370 K (97°C)

9 **a** $\Delta G^{\ominus}_{rxn} = -801 \text{ kJ mol}^{-1}$ **b** $\Delta G^{\ominus}_{rxn} = -101 \text{ kJ mol}^{-1}$
c $\Delta G^{\ominus}_{rxn} = -394 \text{ kJ mol}^{-1}$

10 The two values are virtually the same (174 and 173 kJ mol^{-1}).

Chapter 4 Review questions

4 $\frac{1}{2}H_2(g) + \frac{1}{2}N_2(g) + \frac{3}{2}O_2(g) \rightarrow HNO_3(l); \Delta H^{\ominus}_{rxn} = \Delta H^{\ominus}_f$

5 **a** $2C_6H_6(g) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(g)$
b $\Delta H^{\ominus}_f(C_6H_6) = +177 \text{ kJ mol}^{-1}$

6 $\Delta H^{\ominus}_c(C_4H_{10}) = -2661 \text{ kJ mol}^{-1}$

7 C, MgO

8 $\Delta H^{\ominus}_{lf} = -1020 \text{ kJ mol}^{-1}$

10 SrO

11 Combustion of pentane

13 **a** $NH_4Cl(s) \xrightarrow{aq} NH_4^+(aq) + Cl^-(aq)$
b The entropy will increase as the ammonium chloride dissolves because there is a change of state from solid to aqueous (with associated increase in disorder) and two particles are replacing one.

14 $\Delta S = 10 \text{ J K}^{-1} \text{ mol}^{-1}$

15 $\Delta S(C_3H_8) = 103 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta S(C_4H_{10}) = 158.5 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta S(C_5H_{12}) = 303 \text{ J K}^{-1} \text{ mol}^{-1}$

17 $\Delta H^{\ominus}_{rxn} = -132 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus}_{rxn} = -169 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta G^{\ominus} = -81.6 \text{ kJ mol}^{-1}$

18 $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$
$\Delta H^{\ominus}_{rxn} = -175 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus}_{rxn} = -113 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta G^{\ominus} = -141 \text{ kJ mol}^{-1}$

19 **a** $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$
b $\Delta G^{\ominus}_{rxn} = -14 \text{ kJ mol}^{-1}$

20 **a** There is little change in entropy.
b $\Delta H^{\ominus}_{rxn} = +51.8 \text{ kJ mol}^{-1}$
$\Delta S^{\ominus}_{rxn} = 20.6 \text{ J K}^{-1} \text{ mol}^{-1}$
c $T > 2515$ K

Chapter 4 Test

Part A: Multiple-choice questions

1 C **2** D **3** A **4** D **5** C
6 C **7** D **8** A **9** D **10** B

Chapter 5 Kinetics

Section 5.1

1 **a** first-order **b** zero-order **c** second-order

2 average rate = $7.17 \times 10^{-5} \text{ mol dm}^{-3} \text{ s}^{-1}$

3 **a** Rate doubles. **b** Rate halves.
c Rate increases ninefold.

4 **a** first-order **b** second-order
c Rate = $k[NO]^2[H_2]$ **d** third order
e $k = 8.3 \times 10^4 \text{ mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$

5 **a** $2HI(g) \rightarrow H_2(g) + I_2(g)$ **b** second-order
c Rate = $k[HI]^2$ **d** second-order
e $k = 1.16 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

6 **a** Rate = $k[CH_3OCH_3]$ **b** $k = 4.5 \times 10^{-3} \text{ s}^{-1}$

7 **a** Rate = $k[NO][O_2]^2$

Section 5.2

1 $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

2 **a** A step in a reaction mechanism.
b The step by step process by which a reaction occurs.
c The number of molecules involved in an elementary step; the molecularity of the overall reaction is equal to the molecularity of the rate-determining step.
d It is the slowest step in a reaction mechanism.
e A species that features in a reaction mechanism, but not in the overall equation.

3 **a** 3 (termolecular)
b $H_2(g) + 2NO(g) \rightarrow 2HO\bullet(g) + N_2(g)$
$H_2(g) + 2HO\bullet(g) \rightarrow 2H_2O(g)$
c Intermediate = $HO\bullet(g)$

4 **a** The mechanism doesn't contain a step with a rate expression matching the overall rate expression.
b $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ (one-step process)

5 Rate = $k[NO]^2$

6 **a** bimolecular **b** unimolecular **c** termolecular

7 **a** $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

b Rate = $k[H_2O_2][I^-]$

c bimolecular

d intermediate = $IO^-(aq)$ catalyst = $I^-(aq)$

Section 5.3

2 The transition state is the high-energy state in which bonds in the reactants have started to break and bonds in the products have started to form.

3 fraction = 8.5×10^{-10}

4 **a** $E_a = 10.6$ kJ mol^{-1} **b** $k = 7.34 \times 10^{-4}$ s^{-1}

c $T = 694$ K

5 $E_a = 77.6$ kJ mol^{-1}

6 The magnitude of the rate constant will increase as the absolute temperature increases.

7 **a** $k = 3.67 \times 10^{-11}$ s^{-1} **b** $T = 635$ K

Chapter 5 Review questions

1 **a** It is first-order with respect to A, and second-order with respect to B.

Rate = $k[A][B]^2$

b The probability of four molecules being involved in a single-step reaction is so low as to be non-existent.

c $A + 2B \rightarrow C + E$; slow

$E + A \rightarrow D$; fast

d termolecular

2 **a** False **b** True **c** True **d** False

3 **a** It is a third-order reaction.

b $k = 3.51 \times 10^{3}$ mol^{-2} dm^{6} s^{-1}

4 Reaction A will have the faster rate.

5 The Arrhenius constant (frequency factor, *A*) is a constant related to both collision frequency and the probability that molecules are correctly oriented for reaction.

6 **a** It is first-order with respect to dimethylhydrazine.
It is first-order with respect to I_2.
Rate = $k[(C_2H_5)_2(NH)_2][I_2]$

b $k = 1.03 \times 10^{-4}$ mol^{-1} dm^{3} s^{-1}

c $(C_2H_5)_2(NH)_2(aq) + I_2(aq) \rightarrow 2HI(aq) + (C_2H_5)_2N_2(aq)$

d bimolecular

7 **a** The rate will decrease by a factor of four.

b termolecular

c This could be a one-step process.

d Heating the system would increase *k*.

8 **a** fraction = 1.14×10^{-11} **b** It is more than doubled.

9 **b** bimolecular

10 **a** bimolecular (molecularity = 2)

b $H_2(g) + ICl(g) \rightarrow HCl(g) + HI(g)$; slow

$ICl(g) + HI(g) \rightarrow HCl(g) + I_2(g)$; fast

c HI(g)

11 In one-step processes only.

12 It will apply only to first-order processes.

13 **c** Rate = $k[B]^2$

d $B + B \rightarrow F$ slow (rate-determining step)

$A + F \rightarrow D + G$ fast

$C + G \rightarrow E + B$ fast

14 The units of *k* will depend on how many concentrations are involved in the rate expression.

16 **a** Step 1 **b** unimolecular

17 Adding a catalyst or changing the temperature

18 **a** $A = 0.271$ s^{-1}

b *A* is a constant, so the value of *A* calculated above can be used here.

$k = 4.67 \times 10^{-3}$ s^{-1}

c $T = 276$ K

19 Gradient = $\dfrac{E_a}{R}$

20 $E_a = 133$ kJ mol^{-1} $A = 1.33 \times 10^{6}$

Chapter 5 Test

Part A: Multiple-choice questions

1	A	**2**	B	**3**	D	**4**	D	**5**	A
6	A	**7**	A	**8**	C	**9**	D	**10**	C

Chapter 6 Equilibrium

Section 6.1

1 The equilibrium vapour pressure is the *maximum* vapour pressure of a liquid at a given temperature.

2 The liquid is evaporating and the gas is condensing at the same rate.

3 water < ethanol < ethoxyethane

4 **a** As the temperature of a liquid increases, the equilibrium vapour pressure increases.

b The stronger the intermolecular forces on a liquid, the lower will be the equilibrium vapour pressure.

c The volume of the liquid has no effect.

7 The heat energy breaks the intermolecular bonds in the liquid.

9 The greater the enthalpy of vaporization, the stronger the intermolecular forces.

10 **a** X < Y < W < Z

b The intermolecular forces are stronger in liquid Z than in liquid X.

Section 6.2

1 **a** $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

b Average value of $K_c = 46.7$

2 $K_c = 9.63 \times 10^{-5}$ mol dm^{-3}

3 $[Br_2] = 0.102$ mol dm^{-3}

4 $[HI] = 0.189$ mol dm^{-3}

5 $K_c = 6.06$ mol^{-1} dm^{3}

6 $K_c = 0.0438$ mol dm^{-3}

7 $K_c = 15.3$

8 $K_c = 77.6$

9 $K_c = 1.04 \times 10^{-3}$ mol^{-2} dm^{6}

10 **a** $K_c = \dfrac{[CO][H_2O]}{[CO_2][H_2]}$ **b** $K_c = 3.17$

Chapter 6 Review questions

3 The enthalpy of vaporization, ΔH_{vap}, is the amount of energy required to vaporize one mole of a liquid.

4 As the strength of the intermolecular forces increases, the amount of energy needed to break these bonds (the enthalpy of vaporization) increases.

6 Approximately 56°C.

7 **a** 134 mmHg **b** 55 mmHg **c** 279 mmHg

9 $K_c = 28$

10 **a** Experiment 1: $K_c = 658\ \text{mol}^{-1}\ \text{dm}^3$
Experiment 2: $K_c = 1.75\ \text{mol}^{-1}\ \text{dm}^3$

b Experiment 2 was carried out at a higher temperature than experiment 1.

11 $K_c = 2.22\ \text{mol}^{-1}\ \text{dm}^3$

12 $[I_2] = 2.00 \times 10^{-4}\ \text{mol dm}^{-3}$

13 **a** $[H_2] = 0.786\ \text{mol dm}^{-3}$ **b** K_c would decrease.

14 $K_c = 3.47\ \text{mol}^{-1}\ \text{dm}^3$

15 **a** Experiments 1 and 4 were carried out at 348 K.

b Experiment 3 was carried out at a temperature greater than 348 K.

c Experiment 2 was carried out at a temperature less than 348 K.

16 $K_c = 319\ \text{mol}^{-1}\ \text{dm}^3$

17 $[CO_2]_{eq} = [H_2]_{eq} = 2.13\ \text{mol dm}^{-3}$

18 **a** $K_c = 0.016\ \text{mol dm}^{-3}$

b Concentration fraction = $0.084\ \text{mol dm}^{-3}$

The reaction must proceed to the left in order to reach equilibrium.

Chapter 6 Test

Part A: Multiple-choice questions

1 A 2 A 3 D 4 C 5 D
6 B 7 D 8 C 9 C 10 B

Chapter 7 Acids and bases

Section 7.1

1 **a** pH = 3 **b** pH = 2.20 **c** pH = 4.33
d pH = 13 **e** pH = 12 **f** pH = 11

2 **a** pOH = 5.8 **b** pOH = 11.4
c pOH = 10.3 **d** pOH = 0.52

3 **a** $0.0032\ \text{mol dm}^{-3}$
b $0.0178\ \text{mol dm}^{-3}$
c $1.58 \times 10^{-12}\ \text{mol dm}^{-3}$
d $3.16 \times 10^{-11}\ \text{mol dm}^{-3}$

4 pH = 0.82

5 **a** pH = 0.718 **b** pH = 0.368

6 pH = 13.4 **7** pH = 12.1 **8** pH = 11.4

9 As the water cooled back to 25°C, the pH would increase from around 6 to 7.

10 **a** **i** $[H^+(aq)]$ at 20°C = $8.32 \times 10^{-8}\ \text{mol dm}^{-3}$
ii $[OH^-(aq)]$ at 35°C = $1.41 \times 10^{-7}\ \text{mol dm}^{-3}$
iii $K_w = 3.98 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$

b The self-ionization of water is endothermic.

Section 7.2

1 **a** **i** $HCOOH(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$

ii $K_a = \dfrac{[H_3O^+][HCOO^-]}{[HCOOH]}$

b **i** $HOBr(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OBr^-(aq)$

ii $K_a = \dfrac{[H_3O^+][OBr^-]}{[HOBr]}$

c **i** $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

ii $K_a = \dfrac{[H_3O^+][SO_4^{2-}]}{[H_2SO_4]}$

2 **a** **i** $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3CH_2NH_3^+(aq)$

ii $K_b = \dfrac{[OH^-][CH_3CH_2NH_3^+]}{[CH_2CH_2NH_2]}$

b **i** $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + (CH_3)_3NH^+(aq)$

ii $K_b = \dfrac{[OH^-][(CH_3)NH^+]}{[CH_2CH_2NH_2]}$

c **i** $C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + C_6H_5NH_3^+(aq)$

ii $K_b = \dfrac{[OH^-][C_6H_5NH_3^+]}{[C_6H_5NH_2]}$

3

Monoprotic acid	**K_a (mol dm^{-3})**	**p*Ka***
Phenylethanoic acid	4.90×10^{-5}	**4.31**
Boric acid	**5.75×10^{-10}**	9.24
Bromoethanoic acid	**1.26×10^{-3}**	2.90
Pentanoic acid	1.38×10^{-5}	**4.86**

4

Base	**K_b (mol dm^{-3})**	**pK_b**
Ammonia	**1.78×10^{-5}**	4.75
Methylamine	4.37×10^{-4}	**3.36**
Diethylamine	**8.51×10^{-4}**	3.07
Phenylamine	4.17×10^{-10}	**9.38**

5 pH = 4.76

6 **a** pH = 2.52 **b** pH = 3.47 **c** pH = 1.90

7 **a** **i** pOH = 2.83 **ii** pH = 11.2
b **i** pOH = 3.37 **ii** pH = 10.6

8 **a** **i** Conjugate base of HCOOH is $HCOO^-$.
ii At 298 K, $pK_b(HCOO^-) = 10.25$.

b **i** Conjugate base of C_2H_5COOH is $C_2H_5COO^-$.
ii At 298K, $pK_b(C_2H_5COO^-) = 9.13$.

c **i** Conjugate base of $CH_2ClCOOH$ is CH_2ClCOO^-.
ii At 298K, $pK_b(CH_2ClCOO^-) = 11.14$.

9 $CH_2ClCOOH > HCOOH > C_2H_5COOH$

10 **a** $NH_4^+(aq) + H_2O(l) \rightarrow H_3O + (aq) + NH_3(aq)$

b $K_a = 5.73 \times 10^{-10}\ \text{mol dm}^{-3}$

Section 7.3

1 **a** A buffer solution is a solution containing a mixture of solutes that resists changes in pH when a small amount of an acid or a base is added.

b **i** $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$

ii $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$ then $NH_4^+(aq) \rightarrow H^+(aq) + NH_3(aq)$

2 **a** It is made up of a weak acid and the salt of its conjugate base.
b e.g. ethanoic acid and sodium hydroxide.

3 50 cm^3 of HCl solution containing 0.10 mol of HCl.

4 An acidic buffer: a weak acid and the salt of its conjugate base.
A basic buffer: a weak base and the salt of its conjugate acid.

5 Buffers are used in the human body to maintain a constant pH.

6 pH(buffer) = 5.30

7 pH = 8.95

9 pH(buffer) = 3.75

10 $\frac{[\text{salt}]}{[\text{acid}]} = 1.74$; e.g. 0.10 mol dm^{-3} ethanoic acid and 0.174 mol dm^{-3} sodium ethanoate solution.

Section 7.4

1 $c(CH_3COOH) = 1.23$ mol dm^{-3}

2 $c(Na_3PO_4) = 0.236$ mol dm^{-3}

3 % $C_6H_8O_6$ = 95.8%

4 **a** 0.00180 mol **d** pH ≈ 5 at the equivalence point.

5 **a** pH = 7 **b** $c(HCl) = 0.090$ mol dm^{-3}
c pH = 1.0 **e** 7.5 cm^3

6 **a** 17 cm^3 **b** pH ≈ 8.5

7 **a** curve Y **b** $[H^+(aq)]$ is different.
c The two salt solutions formed in the neutralization reactions have different pHs.
d $pK_a(CH_3COOH) \approx 5$
e $[CH_3COOH] = [HCl] = 0.080$ mol dm^{-3}

9 % $(NH_4^+) = 24.1\%$

Section 7.5

1 **a** $HCl(aq) + KOH(aq) \rightarrow KCl(aq) + H_2O(l)$
b $NaOH(aq) + HCOOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$
c $HNO_3(aq) + NH_3(aq) \rightarrow NH_4NO_3(aq)$
d $CH_3COOH(aq) + CH_3NH_2(aq) \rightarrow CH_3COOCH_3NH_3$

2 **a** pH = 7 **b** pH = 8–9 **c** pH = 4–5

4 $Al(NO_3)_3 > MgSO_4, NaCl > KHCO_3$

6 **a** pH = 7: $HNO_3(aq) + KOH(aq)$
b pH < 7: $HNO_3(aq) + NH_3(aq)$
c pH > 7: $HCOOH(aq) + KOH(aq)$

Section 7.6

3 **a** yellow **b** green **c** blue

5 **a** phenol red or bromothymol blue
b phenolphthalein
c methyl red

8 Methyl orange would not be suitable as the pH at endpoint < pH at equivalence point.

10 **a** $[HCr] >> [Cr^-]$ so the indicator will be yellow.
b $[Cr^-] >> [HCr]$ so the indicator will be red.
c $[HCr] = [Cr^-]$ so the indicator will be orange.

Chapter 7 Review questions

1 **a** pH = 3 **b** pH = 1.93
c pH = 8.93 **d** pH = 6.19

2 **a** [H+] = 10–7
b $[H_3O^+] = 5.62 \times 10^{-3}$ mol dm^{-3}
c $[H_3O^+] = 10$ mol dm^{-3}

3 pH = 0.0792

4 pH = 13.8

5 6.955 dm^3

6 **a** $K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$
b $K_a = \frac{[C_2H_5COO^-][H_3O^+]}{[C_2H_5COOH]}$
c $K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$

7 pH = 6.21

8 pH = 2.95

9 $K_a = 7.26 \times 10^{-4}$ mol dm^{-3}

10 **a** $CH_3CH_2NH_2(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3CH_2NH_3^+(aq)$
b $K_b = \frac{[OH^-][CH_3CH_2NH_3^+]}{[CH_3CH_2NH_2]}$
c At 298 K, $pK_a\ (CH_3CH_2NH_3^+) = 10.73$.

11 **a** $CH_3(CH_2)_2COO^-(aq) + H_2O(l)$
$\rightleftharpoons OH^-(aq) + CH_3(CH_2)2COOH(aq)$
b $K_b = \frac{[OH^-][CH_3(CH_2)_2COOH]}{[CH_3(CH_2)_2COO^-]}$
c pH = 3.06

14 pH = 9.25

15 **a** **i** $NaNO_3$ and H_2O
ii pH = 7
iii phenol red
b **i** NH_4Cl
ii pH < 7
iii methyl red
c **i** CH_3COOK and H_2O
ii pH > 7
iii phenolphthalein

16 **a** a weak acid and a strong base
b pH = 2.8 **c** 28 cm^3
d pH ≅ 8 **e** phenol red

17 **a** $H_2S(aq) + H_2O(l) \rightarrow HS^-(aq) + H_3O^+(aq)$
b $c(H_2S) = 0.10$ mol dm^{-3}
c pH = 4.00

18 **a** $HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$
b The acid form and the conjugate base form of an indicator are distinctly different colours.

19 **a** $K_a = \frac{[H_3O^+][Me^-]}{[HMe]}$ **b** pH = 3.70

20 **a** yellow **b** approximately 8.9

Chapter 7 Test

Part A: Multiple-choice questions

1 B **2** D **3** C **4** A **5** A
6 C **7** A **8** B **9** A **10** B

Chapter 8 Oxidation and reduction

Section 8.1

2 **a** **i** Ag^+ **ii** Na

b VI > I > V > II > III > IV

3 $Ag^+(aq)$ and $Fe^{3+}(aq)$

5 **a** 2.0 V

b $2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

6 **b** **i** Oxidation: $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

ii $Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$

iii 0.57 V

7 **b** $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$

$\frac{1}{2}I_2(s) + e^- \rightarrow I^-(aq)$

$\frac{1}{2}Cl_2(s) + e^- \rightarrow Cl^-(aq)$

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$

c cheaper

8 **a** No reaction occurs.

b $Mg(s) + Zn^{2+}(aq) \rightarrow Mg^{2+}(aq) + Zn(s)$

c No reaction occurs.

d $Na(s) + H_2O(l) \rightarrow Na^+(aq) + \frac{1}{2}H_2(g) + OH^-(aq)$

9 Coating forms in the case of $CuSO_4$ and $AgNO_3$.

Section 8.2

1 **a** $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$ $E^\ominus = +1.23$ V

b $H_2O(l) + e^- \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$ $E^\ominus = -0.83$ V

2 I, III and V

3 **a** Tin at cathode and bromine at anode.

b **iii** Oxidation: $Br^-(aq) \rightarrow \frac{1}{2}Br_2(l) + e^-$

Reduction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

iv Reducing agent: Br^-

Oxidizing agent: Ni^{2+}

v $NiBr_2(aq) \rightarrow Ni(s) + Br_2(l)$

4 **a** $H_2(g)$ and $OH^-(aq)$ at cathode and $O_2(g)$ and $H^+(aq)$ at anode.

5 **a** True **b** False **c** False

d False **e** False

6

Occurrence	Situation
Potassium metal forms at the cathode	Electrolysis of molten potassium bromide
Reduction occurs at the cathode	Any voltaic cell or electrolytic cell
Hydrogen gas forms at the cathode	Electrolysis of aqueous 1 mol dm^{-3} lithium iodide solution
pH decreases at one electrode	Electrolysis of aqueous lead(II) nitrate solution
Chlorine gas forms at the anode	Electrolysis of highly concentrated aqueous potassium chloride solution

7

	Product at anode	Product at cathode
a	$I_2(s)$	$Cu(s)$
b	$O_2(g)$, $H^+(aq)$	$H_2(g)$, $OH^-(aq)$
c	$Cl_2(g)$, $O_2(g)$ and $H^+(aq)$	$H_2(g)$, $OH^-(aq)$
d	$O_2(g)$, $H^+(aq)$	$Zn(s)$

8 **a** Amount of product will be doubled.

b Only 60% of the original amount of product.

c $Fe^{2+}(aq)$ will be made at the cathode instead of $Fe(s)$.

9 II < IV < I < III

10 **b** Medallion should be attached to negative electrode.

d At cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

At anode: $Ag(s) \rightarrow Ag^+(aq) + e^-$

Chapter 8 Review questions

2 $AgNO_3$ and $CuSO_4$

3 **a** iron

4 **a** $Ag(s) \rightarrow Ag^+(aq) + e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

$2Ag(s) + Cu^{2+}(aq) \rightarrow 2Ag^+(aq) + Cu(s)$

b $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

$H^+(aq) + e^- \rightarrow \frac{1}{2}H_2(g)$

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

c No reaction occurs.

d No reaction occurs.

5 **a** Na^+ **b** Sc

6 zinc

7 B, A, C

9 **a** Anode: platinum electrode in the standard hydrogen half cell

Cathode: Palladium metal electrode

b Oxidation: $\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-$

Reduction: $Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$

c Oxidizing agent: $Pd^{2+}(aq)$

Reducing agent: $H_2(g)$

d The platinum electrode in the standard hydrogen half cell is negative and the palladium metal electrode is positive.

e The electrons flow from the hydrogen half cell to the palladium half cell through the connecting wire.

f Negative ions, such as NO_3^-, flow from the palladium half-cell to the hydrogen half cell.

Positive ions, such as H^+ and Na^+, flow from the hydrogen half-cell to the palladium half-cell.

g $Pd^{2+}(aq) + H_2(g) \rightarrow Pd(s) + 2H^+(aq)$

h $E^\ominus$ cell = 0.92 V

10 $2MnO_4^-(aq) + 16H^+(aq) + 10Br^-(aq)$
$\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(l)$

$E^\ominus$ cell = 0.42 V

11 Any metal with $E^\ominus$ more negative than –0.83 V

12 **c** Oxidation: $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$

Reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$

e Overall equation:

$2Ag^+(aq) + H_2O(l) \rightarrow 2Ag(s) + \frac{1}{2}O_2(g) + 2H^+(aq)$

13 The reaction at the anode would be $Ag(s) \rightarrow Ag^+(aq) + e^-$

15

	Product/s at anode	Product/s at cathode
a	$Cl_2(g)$, $O_2(s)$ and $H^+(aq)$	$H_2(g)$ and $OH^-(aq)$
b	$O_2(g)$ and $H^+(aq)$	$H_2(g)$
c	$Br_2(l)$	$H_2(g)$ and $OH^-(aq)$

16 At cathode: $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

At anode: $H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$

17 **a** $AgNO_3(aq)$ or $Ag_2SO_4(aq)$
b $CuI_2(aq)$
c e.g. concentrated NaCl solution

20 **a** $2Br^-(l) \rightarrow Br_2(l) + 2e^-$
b 1.0 mol of potassium
c Current used in the electrolysis experiment; the time for which the current is flowing through the electrolysis cell.

Chapter 8 Test

Part A: Multiple-choice questions

1 B **2** A **3** B **4** C **5** C
6 B **7** A **8** C **9** A **10** C

Chapter 9 Organic chemistry

Section 9.1

1 **a** tetracycline **b** aspirin
c aspirin **d** epinephrine
e cortisone or tetracycline
2 **a** ethanenitrile **b** *N*-methylethanamine
c ethanamide **d** methyl propanoate
3 **a** ethyl propanoate **b** *N*-methylethanamide
c trimethylamine **d** butanenitrile
4 **a** structural isomers
8 Ethanoic acid has the higher boiling point due to the hydrogen bonds between molecules.

Section 9.2

1 **a** An electron-rich atom or group of atoms.
b Examples: hydroxide ion (OH^-) and water (H_2O)
2 bimolecular
3 **a** $CH_3CH_2CH_2CH_2OH$
b $CH_3CH_2CH_2CH_2NH_2$
c $CH_3CH_2CH_2CH_2CN$
5 The reaction produces various types of amine products, not just the required ethylamine.
6 **b** 2-propanamine
8 iodomethane

Section 9.3

1 **b** The rate-determining step depends on the concentration of one species only.
2 **b** The rate-determining step depends on the concentration of two species.
3 **a** **i** hydroxide ion, OH^- **ii** bromide ion, Br^-
iii tertiary **iv** S_N1
4 **a** **i** hydroxide ion, OH^- **ii** chloride ion, Cl^-
iii primary **iv** S_N2
5 II
6 **a** OH^- **b** H_2S
7 **a** S_N1 **c** carbocation
8 **a** S_N2 **b** III
9 $CH_3(CH_2)_4Br$ reacts faster than $(CH_3)_3CH_2CH_2Br$
10 **a** $(CH_3)_3CBr < (CH_3)_3CHBr < CH_3Br$
b $CH_3CH_2Br < (CH_3)_2CHBr < (CH_3)_3CBr$
12 The required order is therefore II > III > I.

Section 9.4

1 **a** **i** hydroxide ion, OH^-
ii bromide ion, Br^-
iii secondary
2 **a** **i** ethoxide ion, $CH_3CH_2O^-$
ii bromide ion, Br^-
iii tertiary
5 **a** S_N2 **b** E2 **c** S_N1 **d** E1 or E2
6 The likely product is CH_3CHCH_2. An elimination reaction has occurred, probably by the E2 mechanism.
7 **a** E2
8 **a** E1 **b** II

Section 9.5

1 **a** Methanol, under acidic conditions
c Examples:

Ethanoic acid has a higher boiling point than methyl ethanoate due to hydrogen bonding between molecules.

Ethanoic acid is acidic; methyl ethanoate is not acidic.

2 **a** ammonia
c Example: Propanoic acid is an acidic substance; propanomide is not acidic.
5 **a** ethanol and methanoic acid
b methanol and propanoic acid
c propanol and methanoic acid
6 **a** ammonia and methanoic acid
b ethylamine and propionic acid
c *N*,*N*-dimethylamine and ethanoic acid
9 Monomers for addition polymers have a carbon–carbon double bond.

Monomers for condensation polymers have at least two functional groups within the molecule.

12 **a** Both have amide links between the monomer units.
b Proteins have many monomers while nylon is a copolymer of only two monomers.

Section 9.7

1 **a** **i** Molecules with the same structural formula but with groups fixed in a different arrangement in space
ii Molecules that are non-superimposable mirror images
iii Molecules with the same chemical formula but different structural formulas
b **i** structural
ii geometrical
iii optical

3 I and IV

5 III, 1-chloro-2-methylpentane

6 **a** It is a beam of light with waves oscillating in a single plane only.

b Each optical isomer of a compound rotates plane polarized light in either a clockwise or anticlockwise direction. A polarimeter is used to determine the direction of rotation of the light.

7 **b** glycine

8 **b** A mixture of compounds will behave as an impure mixture and have a reduced melting point.

Chapter 9 Review questions

2 Examples:

a methyl methanoate **b** *N*-methylethanamide

c pentanenitrile **d** 1-pentanamine

3 **a** S_N2

4 **a** S_N1 **b** S_N2

5 **a** S_N1

7 **a** I **b** II

8 **a** OH^- (or water)

b **i** slower reaction for $(CH_3)_3CBr$

ii slower reaction for $(CH_3)_2CHI$

9 **a** **ii** There is restricted rotation around a C–C double bond.

c **i** OH^- (or water)

11 **a** A polymer formed from more than one type of monomer.

c condensation

14 II, $BrCH_2CHBrCH_3$

16 Alanine, $H_2NCH(CH_3)COOH$ contains a chiral carbon (carbon 1).

18 **b** secondary

c The carbon adjacent to the benzene ring is chiral.

19 **a** 2-bromobutane the molecule contains a chiral carbon, (carbon 2).

b 1-bromobutane; 1-bromo-2-methylpropane; 2-bromo-2-methylpropane

c 1-bromobutane

20 **a** **i** butan-2-ol **ii** substitution

Chapter 9 Test

Part A: Multiple-choice questions

1	B	**2**	A	**3**	B	**4**	B	**5**	A
6	D	**7**	A	**8**	B	**9**	B	**10**	A

GLOSSARY

Activated complex (transition state)
The high-energy state in which bonds in the reactants have started to break and bonds in the products have started to form.

Acid dissociation constant, K_a
A specialised equilibrium constant that is used to describe the dissociation of an acid in aqueous solution:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

Acidic buffer solution
A buffer solution that is made up of a weak acid and the salt of its conjugate base.

Activation energy (E_a)
The minimum amount of energy required to initiate a reaction.

Alloy
A mixture of a metal with one or more other elements.

Amide
A functional group considered as a derivative of the carboxylic acid group in which the –OH of the carboxyl group is replaced by $-NH_2$. It is represented as $-CONH_2$.

Amine
A functional group made up of a nitrogen atom bonded to two hydrogen atoms. This $-NH_2$ group (known as an amino group) replaces one hydrogen in the structure of an alkane.

Arrhenius constant (frequency factor, *A*)
A constant related to both collision frequency and the probability that molecules are correctly orientated for reaction.

Arrhenius equation

$$k = Ae^{-E_a/RT}$$

Aufbau principle
When filling orbitals, electrons are placed into the lowest energy level available.

Axial position
Atoms arranged above and below a central atom in a molecule.

Back titration
A measured excess of reagent is added to the sample being analysed. A reaction occurs completely and usually quickly, and the amount of unreacted reagent in the solution is then determined by direct titration.

Base dissociation constant, K_b
A specialised equilibrium constant that is used to describe the dissociation of a base in aqueous solution:

$$K_b = \frac{[HB^+][OH^-]}{[B]}$$

Basic buffer solution
A buffer solution that is made up of a weak base and the salt of its conjugate acid.

Bimolecular
The molecularity of an elementary process in which two molecules collide and react.

Boiling point
The temperature at which the vapour pressure of a liquid is equal to the external pressure.

Buffer region
The nearly horizontal region of a titration curve which is made up of a mixture of the acid or base being titrated and the salt that has been formed.

Buffer solution
One that resists changes in pH when a small amount of an acid or a base is added.

Carbocation
The positively charged species formed following the heterolytic fission of the C–X bond in a halogenoalkane.

Cell potential
This is equal to the difference between the electrode potentials of the two half-cells of which the cell is composed.

Chemical kinetics
The area of chemistry dealing with reaction rates and how reactions proceed on a molecular level.

Chiral
A chiral molecule and its mirror image cannot be placed so they match exactly. A chiral molecule lacks a plane of symmetry in the molecule. A chiral carbon in a molecule is one that has four different substituents attached.

Collision theory
A theory that explains rates of reactions on a molecular level.

Complex ion
An ion formed when a small, highly charged transition metal ion forms coordinate bonds with a number of ligands.

Concordant
Results which fall within the range of the systematic error of the equipment being used. In particular this is applied to volumes of solution delivered from a burette during a titration.

Condensation
The process in which a gas is changed into a liquid.

Condensation polymerization reaction
A reaction in which monomers with two functional groups react together in condensation reactions to form a polymer chain.

Condensation reaction
A reaction in which two molecules containing functional groups react and join together with the loss of a small molecule (often water).

Coordinate (dative) bond
A covalent bond formed between two atoms, only one of which has provided electrons for the bond.

Coordination number
The number of ligands surrounding a central metal ion in a complex.

Critical pressure
The amount of pressure that is needed to liquefy the gas at the critical temperature.

Critical temperature
The highest temperature at which the vapour can be changed to a liquid by an increase in pressure.

d-block element
An element whose highest energy electrons are filling a d subshell.

Delocalized electrons
Electrons that are free to move within a pi (π) bond.

Dextrorotatory
Optically active compounds that rotate light clockwise (to the right) are said to be dextrorotatory. By convention, rotation to the right is given a plus sign (+).

E1 (unimolecular elimination)
An elimination reaction in which the rate of reaction depends on the concentration of the halogenoalkane only: Rate = k[RX]. In the two-step process a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. A base then removes a hydrogen atom from the carbon atom adjacent to the C–X carbon atom.

E2 (bimolecular elimination)
An elimination reaction in which the rate of reaction depends on the concentration of the halogenoalkane and the base (B): Rate = k[B][RX]. In the one-step process the base attacks a hydrogen atom on the carbon atom adjacent to the C–X carbon atom, forming a transition state with partially formed C–X, B–H and C=C bonds.

Electrodeposition
The coating of a solid product onto an electrode during electrolysis.

Electrolyte
A liquid that can conduct an electric current.

Electromotive force (emf)
The amount of energy delivered to electrons in a voltaic cell under standard conditions.

Electron affinity
The energy change that occurs when an electron is accepted by an atom in the gaseous state to form a negative ion.

Electron configuration
Notation showing main energy levels, subshells and number of electrons in the subshells that represents the electron arrangement in an atom.

Electron sink
Positive terminal of a power source.

Electron source
Negative terminal of a power source.

Electron spin
An intrinsic property of electrons that causes each electron to behave as if it were spinning about an axis. The spinning charge generates a magnetic field whose direction depends on the direction of spin.

Elementary step (elementary process)
A step in a reaction mechanism.

Elimination reaction
The removal of a hydrogen halide HX from a halogenoalkane to form an alkene. Occurs in competition with substitution reactions when a halogenoalkane is reacted with a nucleophile.

Enantiomers
Molecules that are non-superimposable mirror images. Enantiomers rotate plane-polarized light to the same extent, but in opposite directions. One is therefore the (−) or l-form, the other the (+) or d-form.

Endpoint
The point in the titration (pH) at which the indicator changes colour.

Enthalpy of vaporization, ΔH_{vap}
The amount of energy required to vaporize one mole of a liquid.

Enthalpy, H
Heat energy

Entropy, S
The randomness or disorder of a system.

Equatorial position
Atoms arranged around the middle of a molecule at right angles to those in the axial position.

Equilibrium law
The mathematical relationship between the concentrations of products formed in a reaction once equilibrium had been reached and the concentrations of the reactants left behind: $K_c = \frac{[P]^p[Q]^q\ldots}{[A]^a[B]^b\ldots}$ where a, b, p, q are the coefficients of the reactants and products in the equation for the reaction.

Equilibrium vapour pressure
The vapour pressure measured when a dynamic equilibrium exists between condensation and evaporation.

Equivalence point
The point in the titration (pH) at which the acid or base has been completely neutralized, i.e. the acid and the base have reacted in the correct stoichiometric ratio.

Evaporation
The process in which a liquid is transformed into a gas.

First ionization energy
The amount of energy required to remove one mole of electrons from one mole of atoms of an element in the gaseous state.

First-order reaction
A reaction conforming to the rate expression Rate = $k[A]$.

Geometric isomers
Molecules with the same molecular and structural formulas, but with different spatial arrangements of atoms due to restricted rotation about a double bond or a ring structure. They are named *cis* and *trans* according to the positioning of the ligands.

Gibbs free energy, $\Delta G^\ominus$
The energy available to do useful work. It is defined in terms of enthalpy change and entropy change:
$\Delta G^\ominus = \Delta H^\ominus \times T\Delta S^\ominus$.

Half-life
The time taken for the concentration of a reactant to decrease by half.

Half neutralized
The stage of the titration when exactly half of the acid or base being titrated has been neutralized. At this stage $pH = pK_a$ or $pOH = pK_b$.

Heisenberg uncertainty principle
There is a limitation on how precisely we can know the location of a subatomic particle such as an electron.

Henderson equation

$$pH = pK_{in} - \log_{10}\frac{[HIn]}{[In^-]}$$

The equation used to calculated the pH of an indicator.

Heterogeneous catalyst
A catalyst which is in a different state to the reactants it is catalysing.

Heterolytic fission
The breaking of a covalent bond in which one of the atoms involved in the bond retains both electrons from the bond, forming an anion.

Homogeneous catalyst
A catalyst that is in the same state as the reactants it is catalysing.

Homologous series
A family of compounds that share the same general formula.

Hund's rule
Electrons will occupy orbitals singly until all orbitals of a subshell are half-full, then a second electron will be added to the orbitals.

Hybrid orbitals
Orbitals formed when atomic orbitals in the valence shell of an atom are mixed together.

Hybridization
The process of mixing atomic orbitals as atoms approach each other.

Hydrated
Surrounded by water molecules.

Intermediate
A species that features in a reaction mechanism, but not in the overall equation.

Ionic product constant (ionization constant) of water, K_w
A specialised equilibrium constant that is used to describe the acid–base reaction of water molecules in aqueous solution:
$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$ at 25°C.

Ionization isomers
Isomers of a transition metal complex compound in which the elements are the same but the identity of the cation–anion pair varies, e.g. $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.

Lattice enthalpy
The energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

Levorotatory
Optically active compounds that rotate light counterclockwise (to the left) are said to be levorotatory. By convention, rotation to the left is given a minus sign (−).

Ligand
A molecule or ion that has an electron pair it can donate to the central metal ion.

Localized electrons
Electrons in a pi (π) bond which cannot move beyond the two bonding atoms.

Main energy level
A group of subshells with similar energies.

Maxwell–Boltzmann distribution curve
A graph showing the distribution of particle velocities in a gas at a certain temperature.

Mol dm^{-3} s^{-1}
The usual units of rate; equivalent to M s^{-1} or mol L^{-1} s^{-1}.

Molecularity
The number of molecules involved in an elementary step; the molecularity of the overall reaction is equal to the molecularity of the rate-determining step.

Negative charge centres
Pairs of bonding or non-bonding electrons around a central atom.

Nitrile
A functional group made up of a carbon atom triple-bonded to a nitrogen atom, represented as –CN; sometimes called cyanides or cyano compounds.

Nodes
Positions on the electron density graph at which the chance of finding the electron is zero.

Nucleophile
An electron-rich, nucleus-loving species. A reactant with a non-bonding electron pair, or a negative charge that is attracted to a centre of positive charge.

Nucleophilic substitution
A substitution reaction in which a nucleophile is attracted to a positive charge centre.

Octahedral (or square bipyramidal)
A molecular shape (geometry) in which six atoms surround a central atom, with four in an equatorial plane and two in axial positions.

Octahedron
A shape with eight faces, eight edges and six vertices.

Octet rule
That the valence shell of an atom should contain no more than 8 electrons.

Optical isomers
Molecules with the same molecular and structural formulas, but with different spatial arrangements of atoms. Molecules that are not identical to their mirror image; also known as enantiomers.

Orbital
A region of space in which an electron may be found.

Orbital diagram
A diagrammatic representation of electron configuration showing electrons as ↿ and ⇂ arrows in boxes.

Order of a reaction
Indicates the relationship between the concentration of one or more reactants and the reaction rate.

Pauli exclusion principle
Orbitals can hold 0, 1 or 2 electrons, but no more.

Phase
A homogeneous part of a system that is physically distinct from other parts of the system.

Pi (π) bond
Bond between two atoms formed by the sideways overlapping of two orbitals (usually p orbitals).

p*K*a
This is equal to $-\log_{10}K_a$ (*see* acid dissociation constant).

pK_b
This is equal to $-\log_{10}K_b$ (*see* base dissociation constant).

Plane-polarized light
Light with waves oscillating in a single plane.

pOH
This is equal to $-\log_{10}[OH^-]$. It is a quantity that gives an idea of the strength of a base.

Polarimeter
A device in which plane-polarized light is passed through a tube containing a solution of an optically active organic compound. Rotation of the light occurs. The light then passes to a second polarizer—the analyser. By rotating the analyser until the light passes through it, the new plane of polarization can be found. The extent of rotation is then measured as the angle (α) between the original and rotated planes of light.

Polarization
The attraction of the valence electrons of an ion (or atom) to one region of the ion, creating a region of higher electron density.

Positive inductive effect
The tendency of alkyl groups to 'push' the bonding electron pair towards the carbon of the C–X bond in a halogenoalkane. One effect of electron 'pushing' alkyl groups is to allow the positive charge of the central carbon in the carbocation to be dispersed, and so to be more stabilised.

Potential difference
Voltage difference between two points, which will cause current to flow in a closed circuit.

Probability
The chance of an event occurring.

p_x orbital
A dumbbell-shaped orbital aligned with the x-axis.

p_y orbital
A dumbbell-shaped orbital aligned with the y-axis.

p_z orbital
A dumbbell-shaped orbital aligned with the z-axis.

Quantum mechanics
A model of the atom based on quantum theory.

Quantum numbers
A set of numbers that together uniquely describe the position of an electron.

Quantum theory
Energy can be absorbed or emitted in 'packets' or quanta.

Racemic mixture (racemate)
A 50 : 50 mixture of two enantiomers. Racemic mixtures show zero optical activity because the rotation from one enantiomer exactly cancels the opposite rotation by the other enantiomer.

Rate constant (k)
Proportionality constant that features in both the rate expression and the Arrhenius equation.

Rate expression (rate law)
An expression of proportionality between concentration of reactants and rate, having the general form $\text{Rate} = k[R_1]^m[R_2]^n\ldots$

Rate-determining step
The slowest step in a reaction mechanism.

Rate of reaction
The change in the concentration of a reactant or product with respect to time.

Reaction mechanism
A sequence of reaction steps that shows in detail how a reaction possibly occurs.

Reaction pathway
A series of steps that traces the reaction of a reactant to form a product which it cannot form directly.

Resonance
The concept of electrons being delocalized in a pi (π) bond rather than being bound in a double bond.

Resonance hybrid
The average of two resonance structures which represents the observed molecule accurately.

Resonance structures
Different Lewis structures of the same molecule in which double and single bonds alternate.

s orbital
A spherical orbital that has the lowest energy in each main energy level.

Salt hydrolysis
The reaction of a salt with water.

Second-order reaction
A reaction conforming to the rate expression $\text{Rate} = k[A]^2$ or $\text{Rate} = k[A][B]$.

Sigma (σ) bond
Bond between two atoms formed by the end-to-end overlapping of two orbitals.

S_N1 (unimolecular nucleophilic substitution)
A nucleophilic substitution reaction in which the rate of reaction depends on the concentration of one reactant only: $\text{Rate} = k[RX]$. In the two-step process a carbocation forms slowly by the spontaneous heterolytic fission of the C–X bond in the halogenoalkane. The nucleophile then reacts rapidly with the carbocation.

S_N2 (bimolecular nucleophilic substitution)
A nucleophilic substitution reaction in which the rate of reaction depends on the concentrations of both reactants: Rate = k[Nu][RX]. In the one-step process the nucleophile attacks the halogenoalkane, forming a transition state with partially formed C–X and C–Nu bonds.

Spontaneous
Changes or reactions that take place of their own accord.

Square bipyramidal
see Octahedral.

Square planar
A molecular shape (geometry) in which four atoms surround a central atom in a plane.

Stability
The amount of energy possessed by a particle. The greater the stability, the lower the energy of that particle and the lower the chance of it reacting to form another species.

Standard conditions
Temperature of 298 K, solution concentrations of 1 mol dm^{-3} and pressure of 1.01×10^2 kPa.

Standard electrode potential ($E^\ominus$)
The potential difference generated by a voltaic cell when a particular half-cell is connected to a standard hydrogen electrode.

Standard enthalpy change of combustion, $\Delta H_c^\ominus$
The enthalpy change that occurs when one mole of a compound reacts with oxygen in the standard state.

Standard enthalpy change of formation, $\Delta H_f^\ominus$
The enthalpy change that occurs when one mole of a compound is formed from its elements in their standard state.

Standard enthalpy change of reaction, $\Delta H_{rxn}^\ominus$
The enthalpy change that occurs when reactants are converted to products in their standard state.

Standard entropy change of reaction, $\Delta S_{rxn}^\ominus$
The change in the degree of disorder that occurs when reactants are converted to products in their standard state.

Standard free energy change of formation, $\Delta G_f^\ominus$
The free energy change that occurs when one mole of a compound is formed from its elements in their standard state.

Standard free energy change of reaction, $\Delta G_{rxn}^\ominus$
The free energy change when reactants are converted to products in their standard state.

Standard hydrogen electrode (standard hydrogen half-cell)
A half-cell composed of $H^+(aq)/H_2(g)$ under standard conditions.

Standard state
The state in which a substance exists at 298 K and 1.01×10^2 kPa.

Stereoisomers
Molecules with the same molecular and structural formulas, but with different spatial arrangements of atoms. Two types occur, geometric and optical.

Steric hindrance
A change in reactivity due to the spatial arrangement of groups of atoms. It includes the tendency of bulky alkyl groups to crowd the approach of an attacking species, or the crowding by groups of atoms within the same molecule.

Subshell (sub-level)
A group of orbitals all having the same energies.

Successive ionization energies
The amounts of energy required to remove the electrons from one mole of atoms of an element in the gaseous state, one mole of electrons at a time.

Termolecular
The molecularity of an elementary process in which three molecules collide and react.

Titration curve
A graph of pH against volume for a titration of an acid with a base (or a base with an acid).

Transition element
A d-block element that can form at least one stable ion with a partially filled d subshell.

Transition state (activated complex)
The high-energy state in which bonds in the reactants have started to break and bonds in the products have started to form.

Trigonal bipyramid
A molecular shape (geometry) in which five atoms surround a central atom, with three in an equatorial plane and two in axial positions.

Unimolecular
The molecularity of an elementary process in which one molecule reacts and collision with another molecule is not necessary.

Valence-bond theory
A theory in which regions of electron density between two atoms is explained in terms of the overlap of two atomic orbitals.

Vapour
Describes a gas that is below its critical temperature.

Volatile
Evaporates readily from an open dish at room temperature.

Wave-like properties
Physical properties that resemble those of waves rather than particles.

Zero-order reaction
A reaction conforming to the rate expression Rate = k.

INDEX

Page numbers in **bold** refer to key terms in **bold** type in the text. These terms are also defined in the 'terms and definitions' section for each chapter, and in the cumulative glossary.

Atomic number
Element
Atomic mass

1	2											3	4	5	6	7	0
1 **H** 1.01																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.71	29 **Cu** 63.55	30 **Zn** 65.37	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.21	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **§Ac** (227)															

*	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
§	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (254)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)