

Download more books like this one at Gidemy by clicking the link below

https://downloads.gidemy.com

FHSST Authors

The Free High School Science Texts: Textbooks for High School Students Studying the Sciences Chemistry Grades 10 - 12

> Version 0 November 9, 2008

Copyright 2007 "Free High School Science Texts"

Permission **is** granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.2 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled "GNU Free Documentation License".



Did you notice the **FREEDOMS** we've granted you?

Our copyright license is **different!** It grants freedoms rather than just imposing restrictions like all those other textbooks you probably own or use.

- We know people copy textbooks illegally but we would LOVE it if you copied our's go ahead copy to your hearts content, **legally!**
- Publishers' revenue is generated by controlling the market, we don't want any money, go ahead, distribute our books far and wide we DARE you!
- Ever wanted to change your textbook? Of course you have! Go ahead, change ours, make your own version, get your friends together, rip it apart and put it back together the way you like it. That's what we really want!
- Copy, modify, adapt, enhance, share, critique, adore, and contextualise. Do it all, do it with your colleagues, your friends, or alone but get involved! Together we can overcome the challenges our complex and diverse country presents.
- So what is the catch? The only thing you can't do is take this book, make a few changes and then tell others that they can't do the same with your changes. It's share and share-alike and we know you'll agree that is only fair.
- These books were written by volunteers who want to help support education, who want the facts to be freely available for teachers to copy, adapt and re-use. Thousands of hours went into making them and they are a gift to everyone in the education community.

FHSST Core Team

Mark Horner ; Samuel Halliday ; Sarah Blyth ; Rory Adams ; Spencer Wheaton

FHSST Editors

Jaynie Padayachee ; Joanne Boulle ; Diana Mulcahy ; Annette Nell ; René Toerien ; Donovan Whitfield

FHSST Contributors

Rory Adams ; Prashant Arora ; Richard Baxter ; Dr. Sarah Blyth ; Sebastian Bodenstein ; Graeme Broster ; Richard Case ; Brett Cocks ; Tim Crombie ; Dr. Anne Dabrowski ; Laura Daniels ; Sean Dobbs ; Fernando Durrell ; Dr. Dan Dwyer ; Frans van Eeden ; Giovanni Franzoni ; Ingrid von Glehn ; Tamara von Glehn ; Lindsay Glesener ; Dr. Vanessa Godfrey ; Dr. Johan Gonzalez ; Hemant Gopal ; Umeshree Govender ; Heather Gray ; Lynn Greeff ; Dr. Tom Gutierrez ; Brooke Haag ; Kate Hadley ; Dr. Sam Halliday ; Asheena Hanuman ; Neil Hart ; Nicholas Hatcher; Dr. Mark Horner; Robert Hovden; Mfandaidza Hove; Jennifer Hsieh; Clare Johnson ; Luke Jordan ; Tana Joseph ; Dr. Jennifer Klay ; Lara Kruger ; Sihle Kubheka ; Andrew Kubik ; Dr. Marco van Leeuwen ; Dr. Anton Machacek ; Dr. Komal Maheshwari ; Kosma von Maltitz ; Nicole Masureik ; John Mathew ; JoEllen McBride ; Nikolai Meures ; Riana Meyer ; Jenny Miller ; Abdul Mirza ; Asogan Moodaly ; Jothi Moodley ; Nolene Naidu ; Tyrone Negus ; Thomas O'Donnell ; Dr. Markus Oldenburg ; Dr. Jaynie Padayachee ; Nicolette Pekeur ; Sirika Pillay ; Jacques Plaut ; Andrea Prinsloo ; Joseph Raimondo ; Sanya Rajani ; Prof. Sergey Rakityansky ; Alastair Ramlakan ; Razvan Remsing ; Max Richter ; Sean Riddle ; Evan Robinson ; Dr. Andrew Rose ; Bianca Ruddy ; Katie Russell ; Duncan Scott ; Helen Seals ; Ian Sherratt ; Roger Sieloff ; Bradley Smith ; Greg Solomon ; Mike Stringer ; Shen Tian ; Robert Torregrosa ; Jimmy Tseng ; Helen Waugh ; Dr. Dawn Webber ; Michelle Wen ; Dr. Alexander Wetzler ; Dr. Spencer Wheaton ; Vivian White ; Dr. Gerald Wigger ; Harry Wiggins ; Wendy Williams ; Julie Wilson ; Andrew Wood ; Emma Wormauld ; Sahal Yacoob ; Jean Youssef

Contributors and editors have made a sincere effort to produce an accurate and useful resource. Should you have suggestions, find mistakes or be prepared to donate material for inclusion, please don't hesitate to contact us. We intend to work with all who are willing to help make this a continuously evolving resource!

www.fhsst.org

Contents

I	Int	roduction	1
11	M	atter and Materials	3
1	Clas	ssification of Matter - Grade 10	5
	1.1	Mixtures	5
		1.1.1 Heterogeneous mixtures	6
		1.1.2 Homogeneous mixtures	6
		1.1.3 Separating mixtures	7
	1.2	Pure Substances: Elements and Compounds	9
		1.2.1 Elements	9
		1.2.2 Compounds	9
	1.3	Giving names and formulae to substances	10
	1.4	Metals, Semi-metals and Non-metals	13
		1.4.1 Metals	13
		1.4.2 Non-metals	14
		1.4.3 Semi-metals	14
	1.5	Electrical conductors, semi-conductors and insulators	14
	1.6	Thermal Conductors and Insulators	15
	1.7	Magnetic and Non-magnetic Materials	17
	1.8	Summary	18
2	Wha	at are the objects around us made of? - Grade 10	21
	2.1	Introduction: The atom as the building block of matter	21
	2.2	Molecules	21
		2.2.1 Representing molecules	21
	2.3	Intramolecular and intermolecular forces	25
	2.4	The Kinetic Theory of Matter	26
	2.5	The Properties of Matter	28
	2.6	Summary	31
3	The	e Atom - Grade 10	35
	3.1	Models of the Atom	35
		3.1.1 The Plum Pudding Model	35
		3.1.2 Rutherford's model of the atom	36

		3.1.3 The Bohr Model	87
	3.2	How big is an atom?	88
		3.2.1 How heavy is an atom?	88
		3.2.2 How big is an atom?	88
	3.3	Atomic structure	8
		3.3.1 The Electron	39
		3.3.2 The Nucleus	39
	3.4	Atomic number and atomic mass number	0
	3.5	lsotopes	2
		3.5.1 What is an isotope?	2
		3.5.2 Relative atomic mass	5
	3.6	Energy quantisation and electron configuration	6
		3.6.1 The energy of electrons	6
		3.6.2 Energy quantisation and line emission spectra 4	7
		3.6.3 Electron configuration	7
		3.6.4 Core and valence electrons	51
		3.6.5 The importance of understanding electron configuration 5	51
	3.7	Ionisation Energy and the Periodic Table	3
		3.7.1 lons	53
		3.7.2 Ionisation Energy	5
	20	The Amongsment of Atoms in the Davidia Table	6
	3.0	The Arrangement of Atoms in the Periodic Table	0
	3.0	3.8.1 Groups in the periodic table 5	6
	3.0	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5	6 6
	3.9	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5	6 8 9
4	3.9 Ator	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6	56 58 59 3
4	3.9 Ator 4.1	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6	56 58 59 3
4	3.9 Ator 4.1 4.2	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6	 i6 i8 i9 3 i3
4	3.9 Ator 4.1 4.2 4.3	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6	56 58 59 53 53 55
4	3.9 Ator 4.1 4.2 4.3 4.4	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6	3 3 3 3 3 3 3 5 5
4	3.9 Ator 4.1 4.2 4.3 4.4	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 4.4.1 The nature of the covalent bond 6	
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 4.4.1 The nature of the covalent bond 6 Lewis notation and molecular structure 6	3 3 3 3 3 3 5 5 5 5 5 5 5 5 5 5
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 4.4.1 The nature of the covalent bond 6 Lewis notation and molecular structure 6 Electronegativity 7	3 3 3 3 5 5 5 5 7 2
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 4.4.1 The nature of the covalent bond 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7	3 3 3 3 5 5 5 9 2 3
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 sic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i3 i5 i5 i9 i2 i3 i3 i3 i5 i5 i9 i2 i3 i3 i3 i5 i5 i9 i2 i3 i3 i3 i3 i3 i5 i5 i9 i2 i3 i3 <td< td=""></td<>
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 sic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 Ionic Bonding 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i7
4	 3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7 	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 sic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 Ionic Bonding 7 4.7.1 The nature of the ionic bond 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4
4	3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 Ionic Bonding 7 4.7.1 The nature of the ionic bond 7 4.7.2 The crystal lattice structure of ionic compounds 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4 i6 i6 i8 i9 i3 i3 i5 i5 i5 i9 i2 i3 i4 i4 i6
4	 3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7 	3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 sic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 Ionic Bonding 7 4.7.1 The nature of the ionic bond 7 4.7.2 The crystal lattice structure of ionic compounds 7 4.7.3 Properties of lonic Compounds 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4 i6 i6 i8 i9 i3 i3 i5 i5 i5 i9 i2 i3 i4 i4 i6 i6
4	 3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 	The Arrangement of Atoms in the Periodic Table 5 3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 ic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 Ionic Bonding 7 4.7.1 The nature of the ionic bond 7 4.7.2 The crystal lattice structure of ionic compounds 7 4.7.3 Properties of lonic Compounds 7 Metallic bonds 7 7	i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4 i6 i6 i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4 i6 i6 i6 i6 i8 i9 i3 i3 i5 i5 i9 i2 i3 i4 i4 i6 i6 i6 i7
4	 3.9 Ator 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8 	111e Arrangement of Atoms in the Periodic Table 5 3.8.1 Groups in the periodic table 5 3.8.2 Periods in the periodic table 5 Summary 5 sic Combinations - Grade 11 6 Why do atoms bond? 6 Energy and bonding 6 What happens when atoms bond? 6 Covalent Bonding 6 4.4.1 The nature of the covalent bond 6 Lewis notation and molecular structure 6 Electronegativity 7 4.6.1 Non-polar and polar covalent bonds 7 4.6.2 Polar molecules 7 4.7.1 The nature of the ionic bond 7 4.7.2 The crystal lattice structure of ionic compounds 7 4.7.3 Properties of lonic Compounds 7 4.8.1 The nature of the metallic bond 7	6 6 8 9 3 3 5 5 5 9 2 3 4 4 6

	4.9	Writing chemical formulae
		4.9.1 The formulae of covalent compounds
		4.9.2 The formulae of ionic compounds $\ldots \ldots 80$
	4.10	The Shape of Molecules
		4.10.1 Valence Shell Electron Pair Repulsion (VSEPR) theory $\hdots\hdo$
		4.10.2 Determining the shape of a molecule
	4.11	Oxidation numbers
	4.12	Summary
5	Inte	rmolecular Forces - Grade 11 91
	5.1	Types of Intermolecular Forces
	5.2	$Understanding\ intermolecular\ forces \qquad \ldots \qquad \ldots \qquad \ldots \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad .$
	5.3	Intermolecular forces in liquids
	5.4	Summary
6	Solu	tions and solubility - Grade 11 101
	6.1	Types of solutions
	6.2	Forces and solutions
	6.3	Solubility
	6.4	Summary
7	Ator	nic Nuclei - Grade 11 107
	7.1	Nuclear structure and stability
	7.2	The Discovery of Radiation
	7.3	Radioactivity and Types of Radiation
		7.3.1 Alpha ($lpha$) particles and alpha decay
		7.3.2 Beta (β) particles and beta decay $\ldots \ldots 109$
		7.3.3 Gamma (γ) rays and gamma decay
	7.4	Sources of radiation
		7.4.1 Natural background radiation
		7.4.2 Man-made sources of radiation
	7.5	The 'half-life' of an element
	7.6	The Dangers of Radiation
	7.7	The Uses of Radiation
	7.8	Nuclear Fission
		7.8.1 The Atomic bomb - an abuse of nuclear fission
		7.8.2 Nuclear power - harnessing energy
	7.9	Nuclear Fusion
	7.10	Nucleosynthesis
		7.10.1 Age of Nucleosynthesis (225 s - 10^3 s)
		7.10.2 Age of lons $(10^3 \text{ s} - 10^{13} \text{ s})$
		710.2 Are of Atoms (1013 c 1015 c) 122
		$7.10.5$ Age of Atoms $(10^{-5} \text{ s} - 10^{-5} \text{ s})$
		7.10.3 Age of Atoms (10-5 S - 10-5 S) 122 7.10.4 Age of Stars and Galaxies (the universe today) 122

8	Ther	rmal Properties and Ideal Gases - Grade 11 1	25
	8.1	A review of the kinetic theory of matter \ldots \ldots \ldots \ldots \ldots 1	.25
	8.2	Boyle's Law: Pressure and volume of an enclosed gas	.26
	8.3	Charles's Law: Volume and Temperature of an enclosed gas	.32
	8.4	The relationship between temperature and pressure $\ldots \ldots \ldots$.36
	8.5	The general gas equation	.37
	8.6	The ideal gas equation	.40
	8.7	Molar volume of gases	.45
	8.8	Ideal gases and non-ideal gas behaviour	.46
	8.9	Summary	.47
9	Orga	anic Molecules - Grade 12 1	51
	9.1	What is organic chemistry?	.51
	9.2	Sources of carbon	.51
	9.3	Unique properties of carbon	.52
	9.4	Representing organic compounds	.52
		9.4.1 Molecular formula	.52
		9.4.2 Structural formula	.53
		9.4.3 Condensed structural formula	.53
	9.5	Isomerism in organic compounds	.54
	9.6	Functional groups	.55
	9.7	The Hydrocarbons	.55
		9.7.1 The Alkanes	.58
		9.7.2 Naming the alkanes	.59
		9.7.3 Properties of the alkanes	.63
		9.7.4 Reactions of the alkanes	.63
		9.7.5 The alkenes	.66
		9.7.6 Naming the alkenes	.66
		9.7.7 The properties of the alkenes	.69
		9.7.8 Reactions of the alkenes	.69
		9.7.9 The Alkynes	.71
		9.7.10 Naming the alkynes	.71
	9.8	The Alcohols	.72
		9.8.1 Naming the alcohols	.73
		9.8.2 Physical and chemical properties of the alcohols	.75
	9.9	Carboxylic Acids	.76
		9.9.1 Physical Properties	.77
		9.9.2 Derivatives of carboxylic acids: The esters	.78
	9.10	The Amino Group	.78
	9.11	The Carbonyl Group	.78
	9.12	Summary	.79

10	Orga	nnic Macromolecules - Grade 12	185
	10.1	Polymers	185
	10.2	How do polymers form?	186
		10.2.1 Addition polymerisation	186
		10.2.2 Condensation polymerisation	188
	10.3	The chemical properties of polymers	190
	10.4	Types of polymers	191
	10.5	Plastics	191
		10.5.1 The uses of plastics	192
		10.5.2 Thermoplastics and thermosetting plastics	194
		10.5.3 Plastics and the environment	195
	10.6	Biological Macromolecules	196
		10.6.1 Carbohydrates	197
		10.6.2 Proteins	199
		10.6.3 Nucleic Acids	202
	10.7	Summary	204
	C	hemical Change	209
11	Phys	sical and Chemical Change - Grade 10	211
	11.1	Physical changes in matter	211
	11.2	Chemical Changes in Matter	212
		11.2.1 Decomposition reactions	213
		11.2.2 Synthesis reactions	214
	11.3	Energy changes in chemical reactions	217
	11.4	Conservation of atoms and mass in reactions	217
	11.5	Law of constant composition	219
	11.6	Volume relationships in gases	219
	11.7	Summary	220
12	Repr	resenting Chemical Change - Grade 10	223
	12.1	Chemical symbols	223
	12.2	Writing chemical formulae	224
	12.3	Balancing chemical equations	224
		12.3.1 The law of conservation of mass	224
		12.3.2 Steps to balance a chemical equation	226
	12.4	State symbols and other information	230
	12.5	Summary	232
13	Qua	ntitative Aspects of Chemical Change - Grade 11	233

13.1	The Mole	33
13.2	Molar Mass	35
13.3	An equation to calculate moles and mass in chemical reactions	37

13.4	${\sf Molecules \ and \ compounds} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots $
13.5	The Composition of Substances
13.6	Molar Volumes of Gases
13.7	Molar concentrations in liquids
13.8	Stoichiometric calculations
13.9	Summary
11 Eno	ray Changes In Chemical Practicus Grade 11 255
14 LIIE	What causes the energy changes in chemical reactions?
14.2	Exothermic and endothermic reactions
14.2	The heat of reaction 257
14.5	Examples of endethermic and exethermic reactions
14.4	Spontaneous and non spontaneous reactions
14.5	Activities energy and the activited complex
14.0	Activation energy and the activated complex
14.7	Summary
15 Тур	es of Reactions - Grade 11 267
15.1	Acid-base reactions
	15.1.1 What are acids and bases?
	15.1.2 Defining acids and bases
	15.1.3 Conjugate acid-base pairs
	15.1.4 Acid-base reactions
	15.1.5 Acid-carbonate reactions
15.2	Redox reactions
	15.2.1 Oxidation and reduction
	15.2.2 Redox reactions
15.3	Addition, substitution and elimination reactions
	15.3.1 Addition reactions
	15.3.2 Elimination reactions
	15.3.3 Substitution reactions
15.4	Summary
16 Dec	ation Dates Crada 12
10 Rea	Later dusting 207
10.1	Introduction
10.2	Factors affecting reaction rates
10.3	Reaction rates and collision theory
16.4	Measuring Rates of Reaction
16.5	Mechanism of reaction and catalysis
16.6	Chemical equilibrium
	16.6.1 Open and closed systems
	16.6.2 Reversible reactions
	16.6.3 Chemical equilibrium
16.7	The equilibrium constant

353

		16.7.1	Calculating the equilibrium constant $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 30$	5
		16.7.2	The meaning of k_c values	6
	16.8	Le Cha	telier's principle	0
		16.8.1	The effect of concentration on equilibrium $\ldots \ldots \ldots \ldots \ldots \ldots 31$	0
		16.8.2	The effect of temperature on equilibrium	0
		16.8.3	The effect of pressure on equilibrium	2
	16.9	Industr	ial applications	5
	16.10)Summa	ary	6
17	Elect	rochen	nical Reactions - Grade 12 31	9
	17.1	Introdu	ction	9
	17.2	The Ga	Ilvanic Cell	0
		17.2.1	Half-cell reactions in the Zn-Cu cell $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 32$	1
		17.2.2	$Components \ of \ the \ Zn-Cu \ cell \ \ \ldots \ \ \ldots \ \ \ \ \ \ \ \ \ \ \ \ \$	2
		17.2.3	The Galvanic cell	3
		17.2.4	Uses and applications of the galvanic cell $\ldots \ldots \ldots \ldots \ldots \ldots 32$	4
	17.3	The Ele	ectrolytic cell	5
		17.3.1	The electrolysis of copper sulphate $\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 32$	6
		17.3.2	The electrolysis of water	7
		17.3.3	A comparison of galvanic and electrolytic cells	8
	17.4	Standa	rd Electrode Potentials	8
		17.4.1	The different reactivities of metals	9
		17.4.2	Equilibrium reactions in half cells	9
		17.4.3	$Measuring \ electrode \ potential \ . \ . \ . \ . \ . \ . \ . \ . \ . \ $	0
		17.4.4	The standard hydrogen electrode	0
		17.4.5	Standard electrode potentials	3
		17.4.6	Combining half cells	7
		17.4.7	Uses of standard electrode potential $\ldots \ldots \ldots \ldots \ldots \ldots \ldots 33$	8
	17.5	Balanci	ing redox reactions	2
	17.6	Applica	tions of electrochemistry	7
		17.6.1	Electroplating	7
		17.6.2	The production of chlorine	8
		17.6.3	Extraction of aluminium	9
	17.7	Summa	ıry	9

IV Chemical Systems

18	The Water Cycle - Grade 10	355
	18.1 Introduction	355
	18.2 The importance of water	355
	18.3 The movement of water through the water cycle	356
	18.4 The microscopic structure of water	359

18.4.1 The polar nature of water	359
18.4.2 Hydrogen bonding in water molecules	359
18.5 The unique properties of water	360
18.6 Water conservation	363
18.7 Summary	366
19 Global Cycles: The Nitrogen Cycle - Grade 10	369
19.1 Introduction	369
19.2 Nitrogen fixation	369
19.3 Nitrification	371
19.4 Denitrification	372
19.5 Human Influences on the Nitrogen Cycle	372
19.6 The industrial fixation of nitrogen	373
19.7 Summary	374
20 The Hydrosphere - Grade 10	377
20.1 Introduction	377
20.2 Interactions of the hydrosphere	377
20.3 Exploring the Hydrosphere	378
20.4 The Importance of the Hydrosphere	379
20.5 lons in aqueous solution	379
20.5.1 Dissociation in water	380
20.5.2 lons and water hardness	382
20.5.3 The pH scale	382
20.5.4 Acid rain	384
20.6 Electrolytes, ionisation and conductivity	386
20.6.1 Electrolytes	386
20.6.2 Non-electrolytes	387
20.6.3 Factors that affect the conductivity of water	387
20.7 Precipitation reactions	389
20.8 Testing for common anions in solution	391
20.8.1 Test for a chloride	391
20.8.2 Test for a sulphate	391
20.8.3 Test for a carbonate	392
20.8.4 Test for bromides and iodides	392
20.9 Threats to the Hydrosphere	393
20.10Summary	394
21 The Lithosphere - Grade 11	397
21.1 Introduction	397
21.2 The chemistry of the earth's crust	398
21.3 A brief history of mineral use	399
21.4 Energy resources and their uses	400

21.5 Mining and Mineral Processin	g: Gold
21.5.1 Introduction	
21.5.2 Mining the Gold	
21.5.3 Processing the gold or	e
21.5.4 Characteristics and us	es of gold
21.5.5 Environmental impact	s of gold mining 404
21.6 Mining and mineral processing	g: Iron
21.6.1 Iron mining and iron c	re processing
21.6.2 Types of iron	
21.6.3 Iron in South Africa .	
21.7 Mining and mineral processing	g: Phosphates
21.7.1 Mining phosphates .	
21.7.2 Uses of phosphates .	
21.8 Energy resources and their use	es: Coal
21.8.1 The formation of coal	
21.8.2 How coal is removed f	rom the ground
21.8.3 The uses of coal	
21.8.4 Coal and the South A	rican economy
21.8.5 The environmental im	pacts of coal mining
21.9 Energy resources and their use	es: Oil
21.9.1 How oil is formed \ldots	
21.9.2 Extracting oil	
21.9.3 Other oil products	
21.9.4 The environmental im	pacts of oil extraction and use
21.10Alternative energy resources .	
21.11Summary	
22 The Atmosphere - Grade 11	421
22.1 The composition of the atmos	phere
22.2 The structure of the atmosph	ere
22.2.1 The troposphere	
22.2.2 The stratosphere	
22.2.3 The mesosphere	
22.2.4 The thermosphere	
22.3 Greenhouse gases and global	varming
22.3.1 The heating of the atr	nosphere
22.3.2 The greenhouse gases	and global warming
22.3.3 The consequences of g	lobal warming
22.3.4 Taking action to comb	bat global warming
22.4 Summary	

23 The Chemical Industry - Grade 12	435		
23.1 Introduction			
23.2 Sasol	435		
23.2.1 Sasol today: Technology and production	436		
23.2.2 Sasol and the environment	440		
23.3 The Chloralkali Industry	442		
23.3.1 The Industrial Production of Chlorine and Sodium Hydroxide	442		
23.3.2 Soaps and Detergents	446		
23.4 The Fertiliser Industry	450		
23.4.1 The value of nutrients	450		
23.4.2 The Role of fertilisers	450		
23.4.3 The Industrial Production of Fertilisers	451		
23.4.4 Fertilisers and the Environment: Eutrophication	454		
23.5 Electrochemistry and batteries	456		
23.5.1 How batteries work	456		
23.5.2 Battery capacity and energy	457		
23.5.3 Lead-acid batteries	457		
23.5.4 The zinc-carbon dry cell	459		
23.5.5 Environmental considerations	460		
23.6 Summary	461		

A GNU Free Documentation License

467

Part I

Introduction

Part II

Matter and Materials

Chapter 1

Classification of Matter - Grade 10

All the objects that we see in the world around us, are made of **matter**. Matter makes up the air we breathe, the ground we walk on, the food we eat and the animals and plants that live around us. Even our own human bodies are made of matter!

Different objects can be made of different types of matter, or **materials**. For example, a cupboard (an *object*) is made of wood, nails and hinges (the *materials*). The **properties** of the materials will affect the properties of the object. In the example of the cupboard, the strength of the wood and metals make the cupboard strong and durable. In the same way, the raincoats that you wear during bad weather, are made of a material that is waterproof. The electrical wires in your home are made of metal because metals are a type of material that is able to conduct electricity. It is very important to understand the properties of materials, so that we can use them in our homes, in industry and in other applications. In this chapter, we will be looking at different types of materials and their properties.

The diagram below shows one way in which matter can be classified (grouped) according to its different properties. As you read further in this chapter, you will see that there are also other ways of classifying materials, for example according to whether they are good electrical conductors.



Figure 1.1: The classification of matter

1.1 Mixtures

We see mixtures all the time in our everyday lives. A stew, for example, is a mixture of different foods such as meat and vegetables; sea water is a mixture of water, salt and other substances, and air is a mixture of gases such as carbon dioxide, oxygen and nitrogen.



Definition: Mixture

A **mixture** is a combination of more than one substance, where these substances are not bonded to each other.

In a mixture, the substances that make up the mixture:

• are not in a fixed ratio

Imagine, for example, that you have a 250 ml beaker of water. It doesn't matter whether you add 20 g, 40 g, 100 g or any other mass of sand to the water; it will still be called a mixture of sand and water.

• keep their physical properties

In the example we used of the sand and water, neither of these substances has changed in any way when they are mixed together. Even though the sand is in water, it still has the same properties as when it was out of the water.

• can be separated by mechanical means

To separate something by 'mechanical means', means that there is no chemical process involved. In our sand and water example, it is possible to separate the mixture by simply pouring the water through a filter. Something *physical* is done to the mixture, rather than something *chemical*.

Some other examples of mixtures include blood (a mixture of blood cells, platelets and plasma), steel (a mixture of iron and other materials) and the gold that is used to make jewellery. The gold in jewellery is not pure gold but is a mixture of metals. The *carat* of the gold gives an idea of how much gold is in the item.

We can group mixtures further by dividing them into those that are heterogeneous and those that are homogeneous.

1.1.1 Heterogeneous mixtures

A **heterogeneous** mixture does not have a definite composition. Think of a pizza, that is a mixture of cheese, tomato, mushrooms and peppers. Each slice will probably be slightly different from the next because the toppings like the mushrooms and peppers are not evenly distributed. Another example would be granite, a type of rock. Granite is made up of lots of different mineral substances including quartz and feldspar. But these minerals are not spread evenly through the rock and so some parts of the rock may have more quartz than others. Another example is a mixture of oil and water. Although you may add one substance to the other, they will stay separate in the mixture. We say that these heterogeneous mixtures are *non-uniform*, in other words they are not exactly the same throughout.



Definition: Heterogeneous mixture

A heterogeneous mixture is one that is non-uniform, and where the different components of the mixture can be seen.

1.1.2 Homogeneous mixtures

A **homogeneous** mixture has a definite composition, and specific properties. In a homogeneous mixture, the different parts cannot be seen. A solution of salt dissolved in water is an example of a homogeneous mixture. When the salt dissolves, it will spread evenly through the water so that all parts of the solution are the same, and you can no longer see the salt as being separate from the water. Think also of a powdered drink that you mix with water. Provided you give the container a good shake after you have added the powder to the water, the drink will have the same sweet taste for anyone who drinks it, it won't matter whether they take a sip from the top

or from the bottom. The air we breathe is another example of a homogeneous mixture since it is made up of different gases which are in a constant ratio, and which can't be distinguished from each other.



Definition: Homogeneous mixture

A homogeneous mixture is one that is uniform, and where the different components of the mixture cannot be seen.

An **alloy** is a homogeneous mixture of two or more elements, at least one of which is a metal, where the resulting material has metallic properties. Alloys are usually made to improve on the properties of the elements that make them up. Steel for example, is much stronger than iron, which is its main component.

1.1.3 Separating mixtures

Sometimes it is important to be able to separate a mixture. There are lots of different ways to do this. These are some examples:

• Filtration

A piece of filter paper in a funnel can be used to separate a mixture of sand and water.

• Heating / evaporation

Sometimes, heating a solution causes the water to evaporate, leaving the other part of the mixture behind. You can try this using a salt solution.

• Centrifugation

This is a laboratory process which uses the centrifugal force of spinning objects to separate out the heavier substances from a mixture. This process is used to separate the cells and plasma in blood. When the test tubes that hold the blood are spun round in the machine, the heavier cells sink to the bottom of the test tube. Can you think of a reason why it might be important to have a way of separating blood in this way?

• Dialysis

This is an interesting way of separating a mixture because it can be used in some important applications. Dialysis works using a process called *diffusion*. Diffusion takes place when one substance in a mixture moves from an area where it has a high concentration to an area where its concentration is lower. This movement takes place across a semi-permeable membrane. A semi-permeable membrane is a barrier that lets some things move across it, but not others. This process is very important for people whose kidneys are not functioning properly, an illness called *renal failure*.



Normally, healthy kidneys remove waste products from the blood. When a person has renal failure, their kidneys cannot do this any more, and this can be life-threatening. Using dialysis, the blood of the patient flows on one side of a semi-permeable membrane. On the other side there will be a fluid that has no waste products but lots of other important substances such as potassium ions (K^+) that the person will need. Waste products from the blood diffuse from where their concentration is high (i.e. in the person's blood) into the 'clean' fluid on the other side of the membrane. The potassium ions will move in the opposite direction from the fluid into the blood. Through this process, waste products are taken out of the blood so that the person stays healthy.

Activity :: Investigation : The separation of a salt solution Aim:

To demonstrate that a homogeneous salt solution can be separated using physical methods.

Apparatus:

glass beaker, salt, water, retort stand, bunsen burner. **Method:**

- 1. Pour a small amount of water (about 20 ml) into a beaker.
- 2. Measure a teaspoon of salt and pour this into the water.
- 3. Stir until the salt dissolves completely. This is now called a *salt solution*. This salt solution is a homogeneous mixture.
- 4. Place the beaker on a retort stand over a bunsen burner and heat gently. You should increase the heat until the water almost boils.
- 5. Watch the beaker until all the water has evaporated. What do you see in the beaker?



Results:

The water evaporates from the beaker and tiny grains of salt remain at the bottom.

Conclusion:

The sodium chloride solution, which was a homogeneous mixture of salt and water, has been separated using heating and evaporation.

Activity :: Discussion : Separating mixtures

Work in groups of 3-4

Imagine that you have been given a container which holds a mixture of sand, iron filings (small pieces of iron metal), salt and small stones of different sizes. Is this a homogeneous or a heterogeneous mixture? In your group, discuss how you would go about separating this mixture into the four materials that it contains.

Exercise: Mixtures

- 1. Which of the following subtances are mixtures?
 - (a) tap water
 - (b) brass (an alloy of copper and zinc)
 - (c) concrete
 - (d) aluminium
 - (e) Coca cola
 - (f) distilled water
- 2. In each of the examples above, say whether the mixture is homogeneous or heterogeneous

1.2

1.2 Pure Substances: Elements and Compounds

Any material that is not a mixture, is called a **pure substance**. Pure substances include **elements** and **compounds**. It is much more difficult to break down pure substances into their parts, and complex chemical methods are needed to do this.

1.2.1 Elements

An **element** is a chemical substance that can't be divided or changed into other chemical substances by any ordinary chemical means. The smallest unit of an element is the **atom**.



Definition: Element

An element is a substance that cannot be broken down into other substances through chemical means.

There are 109 known elements. Most of these are natural, but some are man-made. The elements we know are represented in the **Periodic Table of the Elements**, where each element is abbreviated to a **chemical symbol**. Examples of elements are magnesium (Mg), hydrogen (H), oxygen (O) and carbon (C). On the Periodic Table you will notice that some of the abbreviations do not seem to match the elements they represent. The element iron, for example, has the chemical formula Fe. This is because the elements were originally given Latin names. Iron has the abbreviation Fe because its Latin name is 'ferrum'. In the same way, sodium's Latin name is 'natrium' (Na) and gold's is 'aurum' (Au).

1.2.2 Compounds

A **compound** is a chemical substance that forms when two or more elements combine in a fixed ratio. Water (H_2O) , for example, is a compound that is made up of two hydrogen atoms for every one oxygen atom. Sodium chloride (NaCl) is a compound made up of one sodium atom for every chlorine atom. An important characteristic of a compound is that it has a **chemical formula**, which describes the ratio in which the atoms of each element in the compound occur.



Definition: Compound

A substance made up of two or more elements that are joined together in a fixed ratio.

Diagram 1.2 might help you to understand the difference between the terms *element*, *mixture* and *compound*. Iron (Fe) and sulfur (S) are two elements. When they are added together, they



Figure 1.2: Understanding the difference between a mixture and a compound

form a *mixture* or iron and sulfur. The iron and sulfur are not joined together. However, if the mixture is heated, a new *compound* is formed, which is called iron sulfide (FeS). In this compound, the iron and sulfur are joined to each other in a ratio of 1:1. In other words, one atom of iron is joined to one atom of sulfur in the compound iron sulfide.



Exercise: Elements, mixtures and compounds

1. In the following table, tick whether each of the substances listed is a *mixture* or a *pure substance*. If it is a mixture, also say whether it is a homogeneous or heterogeneous mixture.

Substance	Mixture or pure	Homogeneous or heterogeneous mixture
fizzy colddrink		
steel		
oxygen		
iron filings		
smoke		
limestone $(CaCO_3)$		

- 2. In each of the following cases, say whether the substance is an element, a mixture or a compound.
 - (a) Cu
 - (b) iron and sulfur
 - (c) Al
 - (d) H_2SO_4
 - (e) SO₃

1.3 Giving names and formulae to substances

It is easy to describe elements and mixtures. But how are compounds named? In the example of iron sulfide that was used earlier, which element is named first, and which 'ending' is given to the compound name (in this case, the ending is -ide)?

The following are some guidelines for naming compounds:

- 1. The compound name will always include the names of the elements that are part of it.
 - A compound of **iron** (Fe) and *sulfur* (S) is **iron** *sulf*ide (FeS)
 - A compound of **potassium** (K) and *bromine* (S) is **potassium** *brom*ide (KBr)
 - A compound of **sodium** (Na) and *chlorine* (Cl) is **sodium** *chlor*ide (NaCl)
- 2. In a compound, the element that is to the left and lower down on the Periodic Table, is used *first* when naming the compound. In the example of NaCl, sodium is a group 1 element on the left hand side of the table, while chlorine is in group 7 on the right of the table. Sodium therefore comes first in the compound name. The same is true for FeS and KBr.
- 3. The **symbols** of the elements can be used to represent compounds e.g. FeS, NaCl and KBr. These are called **chemical formulae**. In these three examples, the ratio of the elements in each compound is 1:1. So, for FeS, there is one atom of iron for every atom of sulfur in the compound.
- 4. A compound may contain **compound ions**. Some of the more common compound ions and their names are shown below.

Name of compound ion	formula
Carbonate	CO_{3}^{2-}
sulphate	$SO_4{}^{2-}$
Hydroxide	OH-
Ammonium	NH_4^+
Nitrate	NO_3^-
Hydrogen carbonate	HCO_3^-
Phosphate	PO_4^{3-}
Chlorate	CIO_3^-
Cyanide	CN^{-}
Chromate	CrO_4^{2-}
Permanganate	MnO_4^-

- 5. When there are only two elements in the compound, the compound is often given a suffix (ending) of -ide. You would have seen this in some of the examples we have used so far. When a non-metal is combined with oxygen to form a negative ion (anion) which then combines with a positive ion (cation) from hydrogen or a metal, then the suffix of the name will be ...ate or ...ite. NO₃⁻ for example, is a negative ion, which may combine with a cation such as hydrogen (HNO₃) or a metal like potassium (KNO₃). The NO₃⁻ anion has the name nitrate. SO₃ in a formula is sulphite, e.g. sodium sulphite (Na₂SO₃). SO₄ is sulphate and PO₄ is phosphate.
- Prefixes can be used to describe the ratio of the elements that are in the compound. You should know the following prefixes: 'mono' (one), 'di' (two) and 'tri' (three).
 - CO (carbon monoxide) There is one atom of oxygen for every one atom of carbon
 - NO₂ (nitrogen dioxide) There are two atoms of oxygen for every one atom of nitrogen
 - SO_3 (sulfur trioxide) There are three atoms of oxygen for every one atom of sulfur

Important:

When numbers are written as 'subscripts' in compounds (i.e. they are written below the element symbol), this tells us how many atoms of that element there are in relation to other elements in the compound. For example in nitrogen dioxide (NO₂) there are two oxygen atoms for every one atom of nitrogen. In sulfur trioxide (SO₃), there are three oxygen atoms for every one atom of sulfur in the compound. Later, when we start looking at chemical equations, you will notice that sometimes there are numbers *before* the compound name. For example, $2H_2O$ means that there are two molecules of water, and that in each molecule there are two hydrogen atoms for every one oxygen atom.

Exercise: Naming compounds

- 1. The formula for calcium carbonate is $CaCO_3$.
 - (a) Is calcium carbonate a mixture or a compound? Give a reason for your answer.
 - (b) What is the ratio of Ca:C:O atoms in the formula?
- 2. Give the name of each of the following substances.
 - (a) KBr
 - (b) HCI
 - (c) KMnO₄
 - (d) NO_2
 - (e) NH_4OH
 - (f) Na_2SO_4
- 3. Give the chemical formula for each of the following compounds.
 - (a) potassium nitrate
 - (b) sodium iodide
 - (c) barium sulphate
 - (d) nitrogen dioxide
 - (e) sodium monosulphate
- 4. Refer to the diagram below, showing sodium chloride and water, and then answer the questions that follow.



- (a) What is the chemical formula for water?
- (b) What is the chemical formula for sodium chloride?
- (c) Label the water and sodium chloride in the diagram.
- (d) Which of the following statements most accurately describes the picture?
 - i. The picture shows a mixture of an element and a compound
 - ii. The picture shows a mixture of two compounds
 - iii. The picture shows two compounds that have been chemically bonded to each other
- 5. What is the formula of this molecule?

$$\begin{array}{cccccccc} H & H \\ | & | \\ H & - C & - C & - O & - H \\ | & | \\ H & H \\ \end{array}$$

A C₆H₂O
B C₂H₆O
C 2C6HO
D ₂CH₆O

1.4 Metals, Semi-metals and Non-metals

The elements in the Periodic Table can also be divided according to whether they are **metals**, **semi-metals** or **non-metals**. On the right hand side of the Periodic Table is a dark 'zigzag' line. This line separates all the elements that are metals from those that are non-metals. Metals are found on the left of the line, and non-metals are those on the right. Metals, semi-metals and non-metals all have their own specific properties.

1.4.1 Metals

Examples of metals include copper (Cu), zinc (Zn), gold (Au) and silver (Ag). On the Periodic Table, the metals are on the left of the zig-zag line. There are a large number of elements that are metals. The following are some of the properties of metals:

• Thermal conductors

Metals are good conductors of heat and are therefore used in cooking utensils such as pots and pans.

• Electrical conductors

Metals are good conductors of electricity, and are therefore used in electrical conducting wires.

• Shiny metallic lustre

Metals have a characteristic shiny appearance and are often used to make jewellery.

Malleable

This means that they can be bent into shape without breaking.

• Ductile

Metals can stretched into thin wires such as copper, which can then be used to conduct electricity.

• Melting point

Metals usually have a high melting point and can therefore be used to make cooking pots and other equipment that needs to become very hot, without being damaged.

You can see how the properties of metals make them very useful in certain applications.

Activity :: Group Work : Looking at metals

- 1. Collect a number of metal items from your home or school. Some examples are listed below:
 - hammer
 - electrical wiring
 - cooking pots
 - jewellery
 - burglar bars
 - coins
- 2. In groups of 3-4, combine your collection of metal objects.
- 3. What is the function of each of these objects?
- 4. Discuss why you think metal was used to make each object. You should consider the properties of metals when you answer this question.

1.4.2 Non-metals

In contrast to metals, non-metals are poor thermal conductors, good electrical insulators (meaning that they do *not* conduct electrical charge) and are neither malleable nor ductile. The non-metals are found on the right hand side of the Periodic Table, and include elements such as sulfur (S), phosphorus (P), nitrogen (N) and oxygen (O).

1.4.3 Semi-metals

Semi-metals have mostly non-metallic properties. One of their distinguishing characteristics is that their conductivity increases as their temperature increases. This is the opposite of what happens in metals. The semi-metals include elements such as silicon (Si) and germanium (Ge). Notice where these elements are positioned in the Periodic Table.

1.5 Electrical conductors, semi-conductors and insulators

An **electrical conductor** is a substance that allows an electrical current to pass through it. Many electrical conductors are metals, but non-metals can also be good conductors. *Copper* is one of the best electrical conductors, and this is why it is used to make conducting wire. In reality, *silver* actually has an even higher electrical conductivity than copper, but because silver is so expensive, it is not practical to use it for electrical wiring because such large amounts are needed. In the overhead power lines that we see above us, *aluminium* is used. The aluminium usually surrounds a steel core which adds tensile strength to the metal so that it doesn't break when it is stretched across distances. Occasionally gold is used to make wire, not because it is a particularly good conductor, but because it is very resistant to surface corrosion. *Corrosion* is when a material starts to deteriorate at the surface because of its reactions with the surroundings, for example oxygen and water in the air.

An **insulator** is a non-conducting material that does not carry any charge. Examples of insulators would be plastic and wood. Do you understand now why electrical wires are normally covered with plastic insulation? **Semi-conductors** behave like insulators when they are cold, and like conductors when they are hot. The elements silicon and germanium are examples of semi-conductors.

Definition: Conductors and insulators

A conductor allows the easy movement or flow of something such as heat or electrical charge through it. Insulators are the opposite to conductors because they *inhibit* or reduce the flow of heat, electrical charge, sound etc through them.

Activity :: Experiment : Electrical conductivity

Aim:

To investigate the electrical conductivity of a number of substances **Apparatus:**

- two or three cells
- light bulb
- crocodile clips
- wire leads
- a selection of test substances (e.g. a piece of plastic, aluminium can, metal pencil sharpener, metal magnet, wood, chalk).



Method:

- 1. Set up the circuit as shown above, so that the test substance is held between the two crocodile clips. The wire leads should be connected to the cells and the light bulb should also be connected into the circuit.
- 2. Place the test substances one by one between the crocodile clips and see what happens to the light bulb.

Results:

Record your results in the table below:

Test substance	Metal/non-metal	Does glow?	bulb	Conductor or insulator

Conclusions:

In the substances that were tested, the metals were able to conduct electricity and the non-metals were not. Metals are good electrical conductors and non-metals are not.

1.6 Thermal Conductors and Insulators

A **thermal conductor** is a material that allows energy in the form of heat, to be transferred within the material, without any movement of the material itself. An easy way to understand this concept is through a simple demonstration.

Activity :: Demonstration : Thermal conductivity Aim: To demonstrate the ability of different substances to conduct heat. Apparatus: You will need two cups (made from the same material e.g. plastic); a metal spoon and a plastic spoon.

Method:

- Pour boiling water into the two cups so that they are about half full.
- At the same time, place a metal spoon into one cup and a plastic spoon in the other.
- Note which spoon heats up more quickly

Results:

The metal spoon heats up more quickly than the plastic spoon. In other words, the metal conducts heat well, but the plastic does not.

Conclusion:

Metal is a good thermal conductor, while plastic is a poor thermal conductor. This explains why cooking pots are metal, but their handles are often plastic or wooden. The pot itself must be metal so that heat from the cooking surface can heat up the pot to cook the food inside it, but the handle is made from a poor thermal conductor so that the heat does not burn the hand of the person who is cooking.

An **insulator** is a material that does not allow a transfer of electricity or energy. Materials that are poor thermal conductors can also be described as being good insulators.

Fac

Water is a better thermal conductor than air and conducts heat away from the body about 20 times more efficiently than air. A person who is not wearing a wetsuit, will lose heat very quickly to the water around them and can be vulnerable to hypothermia. Wetsuits help to preserve body heat by trapping a layer of water against the skin. This water is then warmed by body heat and acts as an insulator. Wetsuits are made out of closed-cell, foam neoprene. Neoprene is a synthetic rubber that contains small bubbles of nitrogen gas when made for use as wetsuit material. Nitrogen gas has very low thermal conductivity, so it does not allow heat from the body (or the water trapped between the body and the wetsuit) to be lost to the water outside of the wetsuit. In this way a person in a wetsuit is able to keep their body temperature much higher than they would otherwise.

Activity :: Investigation : A closer look at thermal conductivity

Look at the table below, which shows the thermal conductivity of a number of different materials, and then answer the questions that follow. The higher the number in the second column, the better the material is at conducting heat (i.e. it is a good thermal conductor). Remember that a material that conducts heat efficiently, will also lose heat more quickly than an insulating material.

Material	Thermal Conductivity (W/m/K)
Silver	429
Stainless steel	16
Standard glass	1.05
Concrete	0.9 - 2
Red brick	0.69
Water	0.58
Snow	0.5 - 0.25
Wood	0.04 - 0.12
Polystyrene	0.03
Air	0.024

Use this information to answer the following questions:

- 1. Name two materials that are good thermal conductors.
- 2. Name two materials that are good insulators.
- 3. Explain why:
 - (a) cooler boxes are often made of polystyrene
 - (b) homes that are made from wood need less internal heating during the winter months.
 - (c) igloos (homes made from snow) are so good at maintaining warm temperatures, even in freezing conditions.

Int Fac

It is a known fact that well-insulated buildings need less energy for heating than do buildings that have no insulation. Two building materials that are being used more and more worldwide, are **mineral wool** and **polystyrene**. Mineral wool is a good insulator because it holds air still in the matrix of the wool so that heat is not lost. Since air is a poor conductor and a good insulator, this helps to keep energy within the building. Polystyrene is also a good insulator and is able to keep cool things cool and hot things hot! It has the added advantage of being resistant to moisture, mould and mildew.

Remember that concepts such as conductivity and insulation are not only relevant in the building, industrial and home environments. Think for example of the layer of blubber or fat that we find in animals. In very cold environments, fat and blubber not only provide protection, but also act as an insulator to help the animal to keep its body temperature at the right level. This is known as *thermoregulation*.

1.7 Magnetic and Non-magnetic Materials

We have now looked at a number of ways in which matter can be grouped, such as into metals, semi-metals and non-metals; electrical conductors and insulators, and thermal conductors and insulators. One way in which we can further group metals, is to divide them into those that are **magnetic** and those that are **non-magnetic**.



Definition: Magnetism

Magnetism is one of the phenomena by which materials exert attractive or repulsive forces on other materials.

A metal is said to be **ferromagnetic** if it can be magnetised (i.e. made into a magnet). If you hold a magnet very close to a metal object, it may happen that its own electrical field will be induced and the object becomes magnetic. Some metals keep their magnetism for longer than others. Look at iron and steel for example. Iron loses its magnetism quite quickly if it is taken away from the magnet. Steel on the other hand will stay magnetic for a longer time. Steel is often used to make permanent magnets that can be used for a variety of purposes.

Magnets are used to sort the metals in a scrap yard, in compasses to find direction, in the magnetic strips of video tapes and ATM cards where information must be stored, in computers and TV's, as well as in generators and electric motors.

Activity :: Investigation : Magnetism

You can test whether an object is magnetic or not by holding another magnet close to it. If the object is attracted to the magnet, then it too is magnetic. Find some objects in your classroom or your home and test whether they are

magnetic or not. Then complete the table below:

Magnetic magnetic	or	non-
	Magnetic magnetic	Magnetic or magnetic

Activity :: Group Discussion : Properties of materials

In groups of 4-5, discuss how our knowledge of the properties of materials has allowed society to:

- develop advanced computer technology
- provide homes with electricity
- find ways to conserve energy

1.8 Summary

- All the objects and substances that we see in the world are made of matter.
- This matter can be classified according to whether it is a mixture or a pure substance.
- A mixture is a combination of one or more substances that are not chemically bonded to each other. Examples of mixtures are air (a mixture of different gases) and blood (a mixture of cells, platelets and plasma).
- The main **characteristics** of mixtures are that the substances that make them up are not in a fixed ratio, they keep their individual properties and they can be separated from each other using mechanical means.

- A heterogeneous mixture is non-uniform and the different parts of the mixture can be seen. An example would be a mixture of sand and salt.
- A homogeneous mixture is uniform, and the different components of the mixture can't be seen. An example would be a salt solution. A salt solution is a mixture of salt and water. The salt dissolves in the water, meaning that you can't see the individual salt particles. They are interspersed between the water molecules. Another example is a metal **alloy** such as steel.
- Mixtures can be **separated** using a number of methods such as filtration, heating, evaporation, centrifugation and dialysis.
- Pure substances can be further divided into elements and compounds.
- An **element** is a substance that can't be broken down into simpler substances through chemical means.
- All the elements are recorded in the **Periodic Table of the Elements**. Each element has its own chemical symbol. Examples are iron (Fe), sulfur (S), calcium (Ca), magnesium (Mg) and fluorine (F).
- A **compound** is a substance that is made up of two or more elements that are chemically bonded to each other in a fixed ratio. Examples of compounds are sodium chloride (NaCl), iron sulfide (FeS), calcium carbonate (CaCO₃) and water (H₂O).
- When **naming compounds** and writing their **chemical formula**, it is important to know the elements that are in the compound, how many atoms of each of these elements will combine in the compound and where the elements are in the Periodic Table. A number of rules can then be followed to name the compound.
- Another way of classifying matter is into **metals** (e.g. iron, gold, copper), **semi-metals** (e.g. silicon and germanium) and **non-metals** (e.g. sulfur, phosphorus and nitrogen).
- **Metals** are good electrical and thermal conductors, they have a shiny lustre, they are malleable and ductile, and they have a high melting point. These properties make metals very useful in electrical wires, cooking utensils, jewellery and many other applications.
- A further way of classifying matter is into electrical conductors, semi-conductors and insulators.
- An electrical conductor allows an electrical current to pass through it. Most metals are good electrical conductors.
- An electrical insulator is not able to carry an electrical current. Examples are plastic, wood, cotton material and ceramic.
- Materials may also be classified as **thermal conductors** or **thermal insulators** depending on whether or not they are able to conduct heat.
- Materials may also be either magnetic or non-magnetic.



Exercise: Summary

- 1. For each of the following **multiple choice** questions, choose *one* correct answer from the list provided.
 - A Which of the following can be classified as a mixture:
 - i. sugar
 - ii. table salt
 - iii. air
 - iv. Iron
 - B An element can be defined as:

- i. A substance that cannot be separated into two or more substances by ordinary chemical (or physical) means
- ii. A substance with constant composition
- iii. A substance that contains two or more substances, in definite proportion by weight
- iv. A uniform substance
- 2. Classify each of the following substances as an *element*, a *compound*, a *solution*(homogeneous mixture), or a *heterogeneous mixture*: salt, pure water, soil, salt water, pure air, carbon dioxide, gold and bronze
- 3. Look at the table below. In the first column (A) is a list of substances. In the second column (B) is a description of the group that each of these substances belongs in. Match up the *substance* in Column A with the *description* in Column B.

Column A	Column B
iron	a compound containing 2 elements
H_2S	a heterogeneous mixture
sugar solution	a metal alloy
sand and stones	an element
steel	a homogeneous mixture

- 4. You are given a test tube that contains a mixture of iron filings and sulfur. You are asked to weigh the amount of iron in the sample.
 - a Suggest one method that you could use to separate the iron filings from the sulfur.
 - b What property of metals allows you to do this?
- 5. Given the following descriptions, write the chemical formula for each of the following substances:
 - a silver metal
 - b a compound that contains only potassium and bromine
 - c a gas that contains the elements carbon and oxygen in a ratio of $1{:}2$
- 6. Give the names of each of the following compounds:
 - a NaBr
 - b $BaSO_4$

c SO_2

- 7. For each of the following materials, say what properties of the material make it important in carrying out its particular function.
 - a tar on roads
 - b iron burglar bars
 - c **plastic** furniture
 - d metal jewellery
 - e clay for building
 - f cotton clothing

Chapter 2

What are the objects around us made of? - Grade 10

2.1 Introduction: The atom as the building block of matter

We have now seen that different materials have different properties. Some materials are metals and some are non-metals; some are electrical or thermal conductors, while others are not. Depending on the properties of these materials, they can be used in lots of useful applications. But what is it exactly that makes up these materials? In other words, if we were to break down a material into the parts that make it up, what would we find? And how is it that a material's microscopic structure is able to give it all these different properties?

The answer lies in the smallest building block of matter: the **atom**. It is the *type* of atoms, and the way in which they are *arranged* in a material, that affects the properties of that substance.

It is not often that substances are found in atomic form. Normally, atoms are bonded to other atoms to form **compounds** or **molecules**. It is only in the *noble gases* (e.g. helium, neon and argon) that atoms are found individually and are not bonded to other atoms. We will look at the reasons for this in a later chapter.

2.2 Molecules

Definition: Molecule

A molecule is a group of two or more atoms that are attracted to each other by relatively strong forces or bonds

Almost everything around us is made up of molecules. *Water* is made up of molecules, each of which has two hydrogen atoms joined to one oxygen atom. *Oxygen* is a molecule that is made up of two oxygen atoms that are joined to one another. Even the food that we eat is made up of molecules that contain atoms of elements such as carbon, hydrogen and oxygen that are joined to one another in different ways. All of these are known as **small molecules** because there are only a few atoms in each molecule. **Giant molecules** are those where there may be millions of atoms per molecule. Examples of giant molecules are *diamonds*, which are made up of millions of carbon atoms bonded to each other, and *metals*, which are made up of millions of metal atoms bonded to each other.

2.2.1 Representing molecules

The structure of a molecule can be shown in many different ways. Sometimes it is easiest to show what a molecule looks like by using different types of **diagrams**, but at other times, we may decide to simply represent a molecule using its **chemical formula** or its written name.

1. Using formulae to show the structure of a molecule

A **chemical formula** is an abbreviated (shortened) way of describing a molecule, or some other chemical substance. In chapter 1, we saw how chemical compounds can be represented using element symbols from the Periodic Table. A chemical formula can also tell us the *number* of atoms of each element that are in a molecule, and their *ratio* in that molecule.

For example, the chemical formula for a molecule of carbon dioxide is:

 CO_2

The formula above is called the **molecular formula** of that compound. The formula tells us that in one molecule of carbon dioxide, there is one atom of carbon and two atoms of oxygen. The ratio of carbon atoms to oxygen atoms is 1:2.



Definition: Molecular formula

A concise way of expressing information about the atoms that make up a particular chemical compound. The molecular formula gives the exact number of each type of atom in the molecule.

A molecule of glucose has the molecular formula:

 $\mathsf{C}_6\mathsf{H}_{12}\mathsf{O}_6$

In each glucose molecule, there are six carbon atoms, twelve hydrogen atoms and six oxygen atoms. The ratio of carbon:hydrogen:oxygen is 6:12:6. We can simplify this ratio to write 1:2:1, or if we were to use the element symbols, the formula would be written as CH_2O . This is called the **empirical formula** of the molecule.



Definition: Empirical formula

This is a way of expressing the *relative* number of each type of atom in a chemical compound. In most cases, the empirical formula does not show the exact number of atoms, but rather the simplest *ratio* of the atoms in the compound.

The empirical formula is useful when we want to write the formula for a *giant molecule*. Since giant molecules may consist of millions of atoms, it is impossible to say exactly how many atoms are in each molecule. It makes sense then to represent these molecules using their empirical formula. So, in the case of a metal such as copper, we would simply write Cu, or if we were to represent a molecule of sodium chloride, we would simply write NaCl.

Chemical formulae therefore tell us something about the *types* of atoms that are in a molecule and the *ratio* in which these atoms occur in the molecule, but they don't give us any idea of what the molecule actually looks like, in other words its *shape*. Another useful way of representing molecules is to use diagrams.

Another type of formula that can be used to describe a molecule is its **structural formula**. A structural formula uses a graphical representation to show a molecule's structure (figure 2.1).

2. Using diagrams to show the structure of a molecule

Diagrams of molecules are very useful because they give us an idea of the *space* that is occupied by the molecule, and they also help us to picture how the atoms are arranged in the molecule. There are two types of diagrams that are commonly used:


Figure 2.1: Diagram showing (a) the molecular, (b) the empirical and (c) the structural formula of isobutane

• Ball and stick models

This is a 3-dimensional molecular model that uses 'balls' to represent atoms and 'sticks' to represent the bonds between them. The centres of the atoms (the balls) are connected by straight lines which represent the bonds between them. A simplified example is shown in figure 2.2.

2.2



Figure 2.2: A ball and stick model of a water molecule

• Space-filling model

This is also a 3-dimensional molecular model. The atoms are represented by multicoloured spheres. Space-filling models of water and ammonia are shown in figures 2.3 and 2.4.

Figures 2.3 and 2.4 are some examples of **simple molecules** that are represented in different ways.



Figure 2.3: A space-filling model and structural formula of a water molecule. Each molecule is made up of two hydrogen atoms that are attached to one oxygen atom. This is a simple molecule.

Figure 2.5 shows the bonds between the carbon atoms in diamond, which is a **giant molecule**. Each carbon atom is joined to four others, and this pattern repeats itself until a complex *lattice* structure is formed. Each black ball in the diagram represents a carbon atom, and each line represents the bond between two carbon atoms.



Diamonds are most often thought of in terms of their use in the jewellery industry. However, about 80% of mined diamonds are unsuitable for use as gemstones and are therefore used in industry because of their strength and hardness. These



Figure 2.4: A space-filling model and structural formula of a molecule of ammonia. Each molecule is made up of one nitrogen atom and three hydrogen atoms. This is a simple molecule.



Figure 2.5: Diagrams showing the microscopic structure of diamond. The diagram on the left shows part of a diamond lattice, made up of numerous carbon atoms. The diagram on the right shows how each carbon atom in the lattice is joined to four others. This forms the basis of the lattice structure. Diamond is a giant molecule.

properties of diamonds are due to the strong covalent bonds betwene the carbon atoms in diamond. The most common uses for diamonds in industry are in cutting, drilling, grinding, and polishing.

Exercise: Atoms and molecules

- 1. In each of the following, say whether the chemical substance is made up of single atoms, simple molecules or giant molecules.
 - (a) ammonia gas (NH₃)
 - (b) zinc metal (Zn)
 - (c) graphite (C)
 - (d) nitric acid (HNO₃)
 - (e) neon gas (Ne₂)
- 2. Refer to the diagram below and then answer the questions that follow:



2.3

- (a) Identify the molecule.
- (b) Write the molecular formula for the molecule.
- (c) Is the molecule a simple or giant molecule?
- 3. Represent each of the following molecules using its *chemical formula*, *structural formula* and *ball and stick model*.
 - (a) H₂
 - (b) NH₃
 - (c) sulfur dioxide

2.3 Intramolecular and intermolecular forces

When atoms join to form molecules, they are held together by **chemical bonds**. The type of bond, and the strength of the bond, depends on the atoms that are involved. These bonds are called **intramolecular forces** because they are bonding forces *inside* a molecule ('intra' means 'within' or 'inside'). Sometimes we simply call these intramolecular forces chemical bonds.



Definition: Intramolecular force

The force between the atoms of a molecule, which holds them together.

Examples of the types of chemical bonds that can exist between atoms inside a molecule are shown below. These will be looked at in more detail in chapter 4.

• Covalent bond

Covalent bonds exist between non-metal atoms e.g. There are covalent bonds between the carbon and oxygen atoms in a molecule of carbon dioxide.

• Ionic bond

lonic bonds occur between non-metal and metal atoms e.g. There are ionic bonds between the sodium and chlorine atoms in a molecule of sodium chloride.

• Metallic bond

Metallic bonds join metal atoms e.g. There are metallic bonds between copper atoms in a piece of copper metal.

Intermolecular forces are those bonds that hold *molecules* together. A glass of water for example, contains many molecules of water. These molecules are held together by intermolecular forces. The strength of the intermolecular forces is important because they affect properties such as *melting point* and *boiling point*. For example, the stronger the intermolecular forces, the higher the melting point and boiling point for that substance. The strength of the intermolecular forces increases as the size of the molecule increases.



Definition: Intermolecular force

A force between molecules, which holds them together.

Diagram 2.6 may help you to understand the difference between intramolecular forces and intermolecular forces.



Figure 2.6: Two representations showing the intermolecular and intramolecular forces in water: space-filling model and structural formula.

It should be clearer now that there are two types of forces that hold matter together. In the case of water, there are intramolecular forces that hold the two hydrogen atoms to the oxygen atom *in each molecule of water*. There are also intramolecular forces *between each of these water molecules*. As mentioned earlier, these forces are very important because they affect many of the *properties of matter* such as boiling point, melting point and a number of other properties. Before we go on to look at some of these examples, it is important that we first take a look at the **Kinetic Theory of Matter**.

Exercise: Intramolecular and intermolecular forces

- 1. Using ammonia gas as an example...
 - (a) Explain what is meant by an *intramolecular* force or *chemical bond*.
 - (b) Explain what is meant by an *intermolecular* force.
- 2. Draw a diagram showing three molecules of carbon dioxide. On the diagram, show where the intramolecular and intermolecular forces are.
- 3. Why is it important to understand the types of forces that exist between atoms and between molecules? Try to use some practical examples in your answer.

2.4 The Kinetic Theory of Matter

The **kinetic theory of matter** is used to explain why matter exists in different *phases* (i.e. solid, liquid and gas), and how matter can change from one phase to the next. The kinetic theory of matter also helps us to understand other properties of matter. It is important to realise that what we will go on to describe is only a *theory*. It cannot be proved beyond doubt, but the fact that it helps us to explain our observations of changes in phase, and other properties of matter, suggests that it probably is more than just a theory.

Broadly, the Kinetic Theory of Matter says that:

- Matter is made up of **particles** that are constantly moving.
- All particles have **energy**, but the energy varies depending on whether the substance is a solid, liquid or gas. Solid particles have the least energy and gas particles have the most amount of energy.

2.4

- The temperature of a substance is a measure of the average kinetic energy of the particles.
- A change in **phase** may occur when the energy of the particles is changed.
- There are **spaces** between the particles of matter.
- There are **attractive forces** between particles and these become stronger as the particles move closer together. These attractive forces will either be intramolecular forces (if the particles are atoms) or intermolecular forces (if the particles are molecules). When the particles are extremely close, repulsive forces start to act.

Table 2.1 summarises the characteristics of the particles that are in each phase of matter.

Property of matter	Gas	Liquid	Gas
Particles	Atoms or molecules	Atoms or molecules	Atoms or molecules
Energy and move- ment of particles	Particles have high energy and are con- stantly moving	Particles have less energy than in the gas phase	Low energy - parti- cles vibrate around a fixed point
Spaces between par- ticles	Large spaces be- cause of high energy	Smaller spaces than in gases	Very little space between particles. Particles are tightly packed together
Attractive forces be- tween particles	Weak forces because of the large distance between particles	Stronger forces than in gas. Liquids can be poured.	Very strong forces. Solids have a fixed volume.
Changes in phase	In general a gas becomes a liquid or solid when it is cooled. Particles have less energy and therefore move closer together so that the attrac- tive forces become stronger, and the gas becomes a liquid or a solid	A liquid becomes a gas if its tempera- ture is increased. It becomes a solid if its temperature de- creases.	Solids become liq- uids or gases if their temperature is in- creased.

Table 2.1: Table summarising the general features of solids, liquids and gases.

Let's look at an example that involves the three phases of water: ice (solid), water (liquid) and water vapour (gas).



Figure 2.7: The three phases of matter

In a solid (e.g. ice), the water molecules have very little energy and can't move away from each other. The molecules are held close together in a regular pattern called a *lattice*. If the ice is

heated, the energy of the molecules increases. This means that some of the water molecules are able to overcome the intermolecular forces that are holding them together, and the molecules move further apart to form *liquid water*. This is why liquid water is able to flow, because the molecules are more free to move than they were in the solid lattice. If the molecules are heated further, the liquid water will become water vapour, which is a gas. Gas particles have lots of energy and are far away from each other. That is why it is difficult to keep a gas in a specific area! The attractive forces between the particles are very weak and they are only loosely held together. Figure 2.8 shows the changes in phase that may occur in matter, and the names that describe these processes.



Figure 2.8: Changes in phase

2.5 The Properties of Matter

Let us now look at what we have learned about chemical bonds, intermolecular forces and the kinetic theory of matter, and see whether this can help us to understand some of the macroscopic properties of materials.

1. Melting point



Definition: Melting point

The temperature at which a *solid* changes its phase or state to become a *liquid*. The reverse process (change in phase from liquid to solid) is called **freezing**.

In order for a solid to melt, the energy of the particles must increase enough to overcome the bonds that are holding the particles together. It makes sense then that a solid which is held together by strong bonds will have a *higher* melting point than one where the bonds are weak, because more energy (heat) is needed to break the bonds. In the examples we have looked at, metals, ionic solids and some atomic lattices (e.g. diamond) have high melting points, whereas the melting points for molecular solids and other atomic lattices (e.g. graphite) are much lower. Generally, the intermolecular forces between molecular solids are *weaker* than those between ionic and metallic solids.

2. Boiling point



Definition: Boiling point

The temperature at which a *liquid* changes its phase to become a *gas*.

When the temperature of a liquid increases, the average kinetic energy of the particles also increases, and they are able to overcome the bonding forces that are holding them in the liquid. When boiling point is reached, *evaporation* takes place and some particles in the liquid become a gas. In other words, the energy of the particles is too great for them to be held in a liquid anymore. The stronger the bonds within a liquid, the higher the boiling point needs to be in order to break these bonds. Metallic and ionic compounds have high boiling points while the boiling point for molecular liquids is lower.

2.5

The data in table 2.2 below may help you to understand some of the concepts we have explained. Not all of the substances in the table are solids at room temperature, so for now, let's just focus on the *boiling points* for each of these substances. Of the substances listed, ethanol has the weakest intermolecular forces, and sodium chloride and mercury have the strongest. What do you notice?

Substance	Melting point (${}^{0}C$)	Boiling point (${}^{0}C$)		
Ethanol (C_2H_6O)	-114,3	78,4		
Water	0	100		
Mercury	-38,83	356,73		
Sodium chloride	801	1465		

Table 2.2: The melting and boiling points for a number of substances

You will have seen that substances such as ethanol, with relatively weak intermolecular forces, have the lowest boiling point, while substances with stronger intermolecular forces such as sodium chloride and mercury, must be heated much more if the particles are to have enough energy to overcome the forces that are holding them together in the liquid or solid phase.

?

Exercise: Forces and boiling point

The table below gives the molecular formula and the boiling point for a number of organic compounds called *alkanes*. Refer to the table and then answer the questions that follow.

Organic compound	Molecular formula	Boiling point (⁰ C)
Methane	CH_2	-161.6
Ethane	C_2H_6	-88.6
Propane	C_3H_8	-45
Butane	C_4H_{10}	-0.5
Pentane	C_5H_{12}	36.1
Hexane	C_6H_{14}	69
Heptane	C_7H_{16}	98.42
Octane	C_8H_{18}	125.52

Data from: http://www.wikipedia.com

- (a) Draw a graph to show the relationship between the number of carbon atoms in each alkane, and its boiling point (Number of carbon atoms will go on the x-axis and boiling point on the y-axis).
- (b) Describe what you see.
- (c) Suggest a reason for what you have observed.
- (d) Why was it enough for us to use 'number of carbon atoms' as a measure of the molecular weight of the molecules?

3. Density and viscosity

Density is a measure of the mass of a substance per unit volume. The density of a solid is generally higher than that of a liquid because the particles are hold much more closely

together and therefore there are more particles packed together in a particular volume. In other words, there is a greater mass of the substance in a particular volume. In general, density increases as the strength of the intermolecular forces increases. **Viscosity** is a measure of how resistant a liquid is to changing its form. Viscosity is also sometimes described as the 'thickness' of a fluid. Think for example of syrup and how slowly it pours from one container into another. Now compare this to how easy it is to pour water. The viscosity of syrup is greater than the viscosity of water. Once again, the stronger the intermolecular forces in the liquid, the greater its viscosity.

It should be clear now that we can explain a lot of the **macroscopic properties** of matter (i.e. the characteristics we can see or observe) by understanding their **microscopic structure** and the way in which the atoms and molecules that make up matter are held together.

Activity :: Investigation : Determining the density of liquids:

Density is a very important property because it helps us to identify different materials. Every material, depending on the elements that make it up, and the arrangement of its atoms, will have a different density.

The equation for density is:

$$\mathsf{Density} = \mathsf{Mass}/\mathsf{Volume}$$

Discussion questions:

To calculate the density of liquids and solids, we need to be able to first determine their mass and volume. As a group, think about the following questions:

- How would you determine the mass of a liquid?
- How would you determine the volume of an irregular solid?

Apparatus:

Laboratory mass balance, 10 ml and 100 ml graduated cylinders, thread, distilled water, two different liquids.

Method:

Determine the density of the distilled water and two liquids as follows:

- 1. Measure and record the mass of a 10 ml graduated cyclinder.
- 2. Pour an amount of distilled water into the cylinder.
- 3. Measure and record the combined mass of the water and cylinder.
- 4. Record the volume of distilled water in the cylinder
- 5. Empty, clean and dry the graduated cylinder.
- 6. Repeat the above steps for the other two liquids you have.
- 7. Complete the table below.

Liquid	Mass (g)	Volume (ml)	Density (g/ml)
Distilled water			
Liquid 1			
Liquid 2			

Activity :: Investigation : Determining the density of irregular solids: Apparatus:

Use the same materials and equpiment as before (for the liquids). Also find a number of solids that have an irregular shape.

Method:

Determine the density of irregular solids as follows:

- 1. Measure and record the mass of one of the irregular solids.
- 2. Tie a piece of thread around the solid.
- 3. Pour some water into a 100 ml graduated cylinder and record the volume.
- 4. Gently lower the solid into the water, keeping hold of the thread. Record the combined volume of the solid and the water.
- 5. Dtermine the volume of the solid by subtracting the combined volume from the original volume of the water only.
- 6. Repeat these steps for the second object.
- 7. Complete the table below.

Solid	Mass (g)	Volume (ml)	Density (g/ml)
Solid 1			
Solid 2			
Solid 3			

2.6 Summary

- The smallest unit of matter is the atom. Atoms can combine to form molecules.
- A molecule is a group of two or more atoms that are attracted to each other by chemical bonds.
- A small molecule consists of a few atoms per molecule. A giant molecule consists of millions of atoms per molecule, for example metals and diamonds.
- The structure of a molecule can be represented in a number of ways.
- The **chemical formula** of a molecule is an abbreviated way of showing a molecule, using the symbols for the elements in the molecule. There are two types of chemical formulae: molecular and empirical formula.
- The **molecular formula** of a molecule gives the exact number of atoms of each element that are in the molecule.
- The **empirical formula** of a molecule gives the relative number of atoms of each element in the molecule.
- Molecules can also be represented using diagrams.
- A **ball and stick** diagram is a 3-dimensional molecular model that uses 'balls' to represent atoms and 'sticks' to represent the bonds between them.
- A space-filling model is also a 3-dimensional molecular model. The atoms are represented by multi-coloured spheres.
- In a molecule, atoms are held together by **chemical bonds** or **intramolecular forces**. Covalent bonds, ionic bonds and metallic bonds are examples of chemical bonds.
- A covalent bond exists between non-metal atoms. An ionic bond exists between nonmetal and metal atoms, and a metallic bond exists between metal atoms.
- Intermolecular forces are the bonds that hold *molecules* together.
- The kinetic theory of matter attempts to explain the behaviour of matter in different phases.
- The theory says that all matter is composed of **particles** which have a certain amount of **energy** which allows them to **move** at different speeds depending on the temperature (energy). There are **spaces** between the particles, and also **attractive forces** between particles when they come close together.

- Understanding chemical bonds, intermolecular forces and the kinetic theory of matter, can help to explain many of the **macroscopic properties** of matter.
- **Melting point** is the temperature at which a *solid* changes its phase to become a *liquid*. The reverse process (change in phase from liquid to solid) is called **freezing**. The stronger the chemical bonds and intermolecular forces in a substance, the higher the melting point will be.
- **Boiling point** is the temperature at which a liquid changes phase to become a gas. The stronger the chemical bonds and intermolecular forces in a substance, the higher the boiling point will be.
- Density is a measure of the mass of a substance per unit volume.
- Viscosity is a measure of how resistant a liquid is to changing its form.

Exercise: Summary exercise

- 1. Give one word or term for each of the following descriptions.
 - (a) The property that determines how easily a liquid flows.
 - (b) The change in phase from liquid to gas.
 - (c) A composition of two or more atoms that act as a unit.
 - (d) Chemical formula that gives the relative number of atoms of each element that are in a molecule.
- 2. For each of the following questions, choose the one correct answer from the list provided.
 - A Ammonia, an ingredient in household cleaners, can be broken down to form one part nitrogen (N) and three parts hydrogen (H). This means that ammonia...
 - i. is a colourless gas
 - ii. is not a compound
 - iii. cannot be an element
 - iv. has the formula N_3H
 - B If one substance A has a melting point that is *lower* than the melting point of substance B, this suggests that...
 - i. A will be a liquid at room temperature.
 - ii. The chemical bonds in substance A are weaker than those in substance B.
 - iii. The chemical bonds in substance A are stronger than those in substance B.
 - iv. B will be a gas at room temperature.
- 3. Boiling point is an important concept to understand.
 - a Define 'boiling point'.
 - b What change in phase takes place when a liquid reaches its boiling point?
 - c What is the boiling point of water?
 - d Use the kinetic theory of matter and your knowledge of intermolecular forces, to explain why water changes phase at this temperature.
- 4. Refer to the table below which gives the melting and boiling points of a number of elements, and then answer the questions that follow. (*Data from http://www.chemicalelements.com*)

Element	Melting point	Boiling point (⁰ C)
copper	1083	2567
magnesium	650	1107
oxygen	-218.4	-183
carbon	3500	4827
helium	-272	-268.6
sulfur	112.8	444.6

- a What state of matter (i.e. solid, liquid or gas) will each of these elements be in at room temperature?
- b Which of these elements has the strongest forces between its atoms? Give a reason for your answer.
- c Which of these elements has the weakest forces between its atoms? Give a reason for your answer.

Chapter 3

The Atom - Grade 10

We have now looked at many examples of the types of matter and materials that exist around us, and we have investigated some of the ways that materials are classified. But what is it that makes up these materials? And what makes one material different from another? In order to understand this, we need to take a closer look at the building block of matter, the **atom**. Atoms are the basis of all the structures and organisms in the universe. The planets, the sun, grass and trees, the air we breathe, and people are all made up of different combinations of atoms.

3.1 Models of the Atom

It is important to realise that a lot of what we know about the structure of atoms has been developed over a long period of time. This is often how scientific knowledge develops, with one person building on the ideas of someone else. We are going to look at how our modern understanding of the atom has evolved over time.

The idea of atoms was invented by two Greek philosophers, Democritus and Leucippus in the fifth century BC. The Greek word $\alpha \tau o \mu o \nu$ (atom) means *indivisible* because they believed that atoms could not be broken into smaller pieces.

Nowadays, we know that atoms are made up of a *positively charged* **nucleus** in the centre surrounded by *negatively charged* **electrons**. However, in the past, before the structure of the atom was properly understood, scientists came up with lots of different *models* or *pictures* to describe what atoms look like.



Definition: Model

A model is a representation of a system in the real world. Models help us to understand systems and their properties. For example, an *atomic model* represents what the structure of an atom *could* look like, based on what we know about how atoms behave. It is not necessarily a true picture of the exact structure of an atom.

3.1.1 The Plum Pudding Model

After the electron was discovered by J.J. Thomson in 1897, people realised that atoms were made up of even smaller particles than they had previously thought. However, the atomic nucleus had not been discovered yet, and so the 'plum pudding model' was put forward in 1904. In this model, the atom is made up of negative electrons that float in a soup of positive charge, much like plums in a pudding or raisins in a fruit cake (figure 3.1). In 1906, Thomson was awarded the Nobel Prize for his work in this field. However, even with the Plum Pudding Model, there was still no understanding of how these electrons in the atom were arranged.



Figure 3.1: A schematic diagram to show what the atom looked like according to the Plum Pudding model

The discovery of **radiation** was the next step along the path to building an accurate picture of atomic structure. In the early twentieth century, Marie Curie and her husband discovered that some elements (the *radioactive* elements) emit particles, which are able to pass through matter in a similar way to X-rays (read more about this in chapter 7). It was Ernest Rutherford who, in 1911, used this discovery to revise the model of the atom.

3.1.2 Rutherford's model of the atom

Radioactive elements emit different types of particles. Some of these are positively charged alpha (α) particles. Rutherford carried out a series of experiments where he bombarded sheets of gold foil with these particles, to try to get a better understanding of where the positive charge in the atom was. A simplified diagram of his experiment is shown in figure 3.2.



Figure 3.2: Rutherford's gold foil experiment. Figure (a) shows the path of the α particles after they hit the gold sheet. Figure (b) shows the arrangement of atoms in the gold sheets, and the path of the α particles in relation to this.

Rutherford set up his experiment so that a beam of alpha particles was directed at the gold sheets. Behind the gold sheets, was a screen made of zinc sulfide. This screen allowed Rutherford to see where the alpha particles were landing. Rutherford knew that the *electrons* in the gold atoms would not really affect the path of the alpha particles, because the mass of an electron is so much smaller than that of a proton. He reasoned that the positively charged *protons* would be the ones to *repel* the positively charged alpha particles and alter their path.

What he discovered was that most of the alpha particles passed through the foil undisturbed, and could be detected on the screen directly behind the foil (A). Some of the particles ended up being slightly deflected onto other parts of the screen (B). But what was even more interesting was that some of the particles were deflected straight back in the direction from where they had come (C)! These were the particles that had been repelled by the positive protons in the gold atoms. If the Plum Pudding model of the atom were true, then Rutherford would have expected much more repulsion since the positive charge, according to that model, is distributed throughout the atom. But this was not the case. The fact that most particles passed straight through suggested that the positive charge was concentrated in one part of the atom only.

Rutherford's work led to a change in ideas around the atom. His new model described the atom as a tiny, dense, positively charged core called a nucleus, surrounded by lighter, negatively charged electrons. Another way of thinking about this model was that the atom was seen to be like a mini solar system where the electrons orbit the nucleus like planets orbiting around the sun. A simplified picture of this is shown in figure 3.3.



Figure 3.3: Rutherford's model of the atom

3.1.3 The Bohr Model

There were, however, some problems with this model: for example it could not explain the very interesting observation that atoms only emit light at certain wavelengths or frequencies. Niels Bohr solved this problem by proposing that the electrons could only orbit the nucleus in certain special orbits at different energy levels around the nucleus. The exact energies of the orbitals in each energy level depends on the type of atom. Helium for example, has different energy levels to Carbon. If an electron jumps down from a higher energy level to a lower energy level, then light is emitted from the atom. The energy of the light emitted is the same as the gap in the energy between the two energy levels. You can read more about this in section 3.6. The distance between the nucleus and the electron in the lowest energy level of a hydrogen atom is known as the **Bohr radius**.



Light has the properties of both a particle *and* a wave! Einstein discovered that light comes in energy packets which are called **photons**. When an electron in an atom changes energy levels, a photon of light is emitted. This photon has the same energy as the difference between the two electron energy levels.

3.2 How big is an atom?

It is difficult sometimes to imagine the size of an atom, or its mass, because we cannot see them, and also because we are not used to working with such small measurements.

3.2.1 How heavy is an atom?

It is possible to determine the mass of a single atom in kilograms. But to do this, you would need very modern mass spectrometers, and the values you would get would be very clumsy and difficult to use. The mass of a carbon atom, for example, is about 1.99×10^{-26} kg, while the mass of an atom of hydrogen is about 1.67×10^{-27} kg. Looking at these very small numbers makes it difficult to compare how much bigger the mass of one atom is when compared to another.

To make the situation simpler, scientists use a different unit of mass when they are describing the mass of an atom. This unit is called the **atomic mass unit** (amu). We can abbreviate (shorten) this unit to just 'u'. If we give carbon an atomic mass of 12 u, then the mass of an atom of hydrogen will be 1 u. You can check this by dividing the mass of a carbon atom in kilograms (see above) by the mass of a hydrogen atom in kilograms (you will need to use a calculator for this!). If you do this calculation, you will see that the mass of a carbon atom is twelve times greater than the mass of a hydrogen atom. When we use atomic mass units instead of kilograms, it becomes easier to see this. Atomic mass units are therefore not giving us the *actual* mass of an atom, but rather its mass *relative* to the mass of other atoms in the Periodic Table. The atomic masses of some elements are shown in table 3.1 below.

Element	Atomic mass (u)
Nitrogen (N)	14
Bromine (Br)	80
Magnesium (Mg)	24
Potassium (K)	39
Calcium (Ca)	40
Oxygen (O)	16

Table 3.1: The atomic mass of a number of elements

The actual value of 1 atomic mass unit is 1.67×10^{-24} g or 1.67×10^{-27} kg. This is a very tiny mass!

3.2.2 How big is an atom?

 $\begin{array}{l} {\it pm stands for} \\ {\it picometres. 1} \\ {\it pm } = \ 10^{-12} \\ {\it m} \end{array}$

Atomic diameter also varies depending on the element. On average, the diameter of an atom ranges from 100 pm (Helium) to 670 pm (Caesium). Using different units, 100 pm = 1 Angstrom, and 1 Angstrom = 10^{-10} m. That is the same as saying that 1 Angstrom = 0,0000000010 m or that 100 pm = 0,0000000010 m! In other words, the diameter of an atom ranges from 0.0000000010 m to 0.0000000067 m. This is very small indeed.

3.3 Atomic structure

As a result of the models that we discussed in section 3.1, scientists now have a good idea of what an atom looks like. This knowledge is important because it helps us to understand things like why materials have different properties and why some materials bond with others. Let us now take a closer look at the microscopic structure of the atom.

So far, we have discussed that atoms are made up of a positively charged **nucleus** surrounded by one or more negatively charged **electrons**. These electrons orbit the nucleus.

3.3.1 The Electron

The electron is a very light particle. It has a mass of 9.11×10^{-31} kg. Scientists believe that the electron can be treated as a *point particle* or *elementary particle* meaning that it can't be broken down into anything smaller. The electron also carries one unit of **negative** electric charge which is the same as 1.6×10^{-19} C (Coulombs).

3.3.2 The Nucleus

Unlike the electron, the nucleus *can* be broken up into smaller building blocks called **protons** and **neutrons**. Together, the protons and neutrons are called **nucleons**.

The Proton

Each proton carries one unit of **positive** electric charge. Since we know that atoms are *electrically neutral*, i.e. do not carry any extra charge, then the number of protons in an atom has to be the same as the number of electrons to balance out the positive and negative charge to zero. The total positive charge of a nucleus is equal to the number of protons in the nucleus. The proton is much heavier than the electron (10 000 times heavier!) and has a mass of 1.6726×10^{-27} kg. When we talk about the atomic mass of an atom, we are mostly referring to the combined mass of the protons and neutrons, i.e. the nucleons.

The Neutron

The neutron is electrically neutral i.e. it carries no charge at all. Like the proton, it is much heavier than the electron and its mass is 1.6749×10^{-27} kg (slightly heavier than the proton).



Rutherford predicted (in 1920) that another kind of particle must be present in the nucleus along with the proton. He predicted this because if there were only positively charged protons in the nucleus, then it should break into bits because of the repulsive forces between the like-charged protons! Also, if protons were the only particles in the nucleus, then a helium nucleus (atomic number 2) would have two protons and therefore only twice the mass of hydrogen. However, it is actually *four* times heavier than hydrogen. This suggested that there must be something else inside the nucleus as well as the protons. To make sure that the atom stays electrically neutral, this particle would have to be neutral itself. In 1932 James Chadwick discovered the neutron and measured its mass.

	proton	neutron	electron	
Mass (kg)	1.6726×10^{-27}	1.6749×10^{-27}	9.11×10^{-31}	
Units of charge	+1	0	-1	
Charge (C)	1.6×10^{-19}	0	-1.6×10^{-19}	

Table 3.2: Summary of the particles inside the atom



Unlike the electron which is thought to be a *point particle* and unable to be broken up into smaller pieces, the proton and neutron **can** be divided. Protons and neutrons are built up of smaller particles called *quarks*. The proton and neutron are made up of 3 quarks each.

3.4 Atomic number and atomic mass number

The chemical properties of an element are determined by the charge of its nucleus, i.e. by the *number of protons*. This number is called the **atomic number** and is denoted by the letter **Z**.



Definition: Atomic number (Z) The number of protons in an atom

The mass of an atom depends on how many nucleons its nucleus contains. The number of nucleons, i.e. the total number of protons *plus* neutrons, is called the **atomic mass number** and is denoted by the letter A.



Definition: Atomic mass number (A) The number of protons and neutrons in the nucleus of an atom

Standard notation shows the chemical symbol, the atomic mass number and the atomic number of an element as follows:



For example, the iron nucleus which has 26 protons and 30 neutrons, is denoted as

 ${}^{56}_{26}$ Fe ,

where the total nuclear charge is Z = 26 and the mass number A = 56. The number of neutrons is simply the difference N = A - Z.



Important:

Don't confuse the notation we have used above, with the way this information appears on the Periodic Table. On the Periodic Table, the atomic number usually appears in the top lefthand corner of the block or immediately above the element's symbol. The number below the element's symbol is its **relative atomic mass**. This is not exactly the same as the atomic mass number. This will be explained in section 3.5. The example of iron is used again below.



You will notice in the example of iron that the atomic mass number is more or less the same as its atomic mass. Generally, an atom that contains n protons and neutrons (i.e. Z = n), will have a mass approximately equal to n u. The reason is that a C-12 atom has 6 protons, 6 neutrons and 6 electrons, with the protons and neutrons having about the same mass and the electron mass being negligible in comparison.

Exercise: The structure of the atom

- 1. Explain the meaning of each of the following terms:
 - (a) nucleus
 - (b) electron
 - (c) atomic mass
- 2. Complete the following table: (Note: You will see that the atomic masses on the Periodic Table are not *whole numbers*. This will be explained later. For now, you can round off to the nearest whole number.)

Element	Atomic mass	Atomic number	Number of pro-	Number of elec-	Number of neu-
			tons	trons	trons
Mg	24	12			
0			8		
		17			
Ni				28	
	40				20
Zn					
					0
С	12			6	

- 3. Use standard notation to represent the following elements:
 - (a) potassium
 - (b) copper
 - (c) chlorine
- 4. For the element ${}^{35}_{17}$ Cl, give the number of ...
 - (a) protons
 - (b) neutrons
 - (c) electrons
 - ... in the atom.

- 3.5
- 5. Which of the following atoms has 7 electrons?
 - (a) ${}_{2}^{5}$ He
 - (b) ${}^{13}_{6}C$
 - (c) ⁷₃Li
 - (d) $^{15}_{7}N$
- 6. In each of the following cases, give the number or the element symbol represented by 'X'.
 - (a) $^{40}_{18}X$
 - (b) $\frac{x}{20}$ Ca
 - (c) $\frac{31}{x}$ P
- 7. Complete the following table:

	Α	Z	Ν
$^{235}_{92}$ U			
$^{238}_{92}$ U			

In these two different forms of Uranium...

- (a) What is the *same*?
- (b) What is *different*?

Uranium can occur in different forms, called *isotopes*. You will learn more about isotopes in section 3.5.

3.5 Isotopes

3.5.1 What is an isotope?

If a few neutrons are added to or removed from a nucleus, the chemical properties of the atom will stay the same because its charge is still the same. Therefore, the chemical properties of an element depend on the number of protons inside the atom. This means that such an atom should remain in the same place in the Periodic table. For example, no matter how many neutrons we add or subtract from a nucleus with 6 protons, that element will *always* be called carbon and have the element symbol C (see the Table of Elements). Atoms which have the same number of protons, but a different number of neutrons, are called **isotopes**.



Definition: Isotope

The **isotope** of a particular element, is made up of atoms which have the same number of protons as the atoms in the orginal element, but a different number of neutrons.

The different isotopes of an element have the same atomic number Z but different mass numbers A because they have a different number of neutrons N. The chemical properties of the different isotopes of an element are the same, but they might vary in how stable their nucleus is. Note that if an element is written for example as C-12, the '12' is the atomic mass of that atom. So, Cl-35 has an atomic mass of 35 u, while Cl-37 has an atomic mass of 37 u.



In Greek, "same place" reads as $i\sigma\sigma\varsigma \ \tau \delta\pi\sigma\varsigma$ (isos topos). This is why atoms which have the same number of protons, but different numbers of neutrons, are called *isotopes*. They are in the same place on the Periodic Table!



Worked Example 1: Isotopes

Question: For the element $^{234}_{92}$ U (uranium), use standard notation to describe:

- 1. the isotope with 2 fewer neutrons
- 2. the isotope with 4 more neutrons

Answer

Step 1 : Go over the definition of isotope

We know that isotopes of any element have the *same* number of protons (same atomic number) in each atom which means that they have the same chemical symbol. However, they have a different number of neutrons, and therefore a different mass number.

Step 2 : Rewrite the notation for the isotopes

Therefore, any isotope of uranium will have the symbol:

U

Also, since the number of protons in uranium isotopes is always the same, we can write down the atomic number:

 $_{92}\mathrm{U}$

Now, if the isotope we want has 2 fewer neutrons than $^{234}_{92}\rm U$, then we take the original mass number and subtract 2, which gives:

 $^{232}_{92}{\rm U}$

Following the steps above, we can write the isotope with 4 more neutrons as:

 ${}^{238}_{92}\mathrm{U}$



Worked Example 2: Isotopes

Question: Which of the following are isotopes of ${}^{40}_{20}Ca$?

- ⁴⁰₁₉K
- ${}^{42}_{20}$ Ca
- ${}^{40}_{18}{
 m Ar}$

Answer

Step 1 : Go over the definition of isotope:

We know that isotopes have the same atomic number but different mass numbers.

Step 2 : Determine which of the elements listed fits the definition of an isotope.

You need to look for the element that has the same atomic number but a different atomic mass number. The only element is $\frac{12}{20}$ Ca. What is different is that there are 2 more neutrons than in the original element.



Worked Example 3: Isotopes

Question: For the sulfur isotope ${}^{33}_{16}S$, give the number of...

- 1. protons
- 2. nucleons
- 3. electrons
- 4. neutrons

Answer

Step 1: Determine the number of protons by looking at the atomic number, Z.

Z = 16, therefore the number of protons is 16 (answer to (a)).

Step 2 : Determine the number of nucleons by looking at the atomic mass number, $\ensuremath{\mathsf{A}}.$

A = 33, therefore the number of nucleons is 33 (answer to (b)).

Step 3 : Determine the number of electrons

The atom is neutral, and therefore the number of electrons is the same as the number of protons. The number of electrons is 16 (answer to (c)).

Step 4 : Calculate the number of neutrons

$$N = A - Z = 33 - 16 = 17$$

The number of neutrons is 17 (answer to (d)).

Exercise: Isotopes

- 1. Atom A has 5 protons and 5 neutrons, and atom B has 6 protons and 5 neutrons.
 - These atoms are...
 - (a) allotropes
 - (b) isotopes
 - (c) isomers
 - (d) atoms of different elements
- 2. For the sulfur isotopes, ${}^{32}_{16}S$ and ${}^{34}_{16}S$, give the number of...
 - (a) protons
 - (b) nucleons
 - (c) electrons
 - (d) neutrons
- 3. Which of the following are isotopes of Cl^{35} ?
 - (a) $^{17}_{35}$ Cl
 - (b) ³⁵₁₇Cl
 - (c) ³⁷₁₇Cl
- 4. Which of the following are isotopes of U-235? (X represents an element symbol)
 - (a) $^{238}_{92}$ X
 - (b) $\frac{238}{90}$ X
 - (c) $\frac{235}{92}$ X

3.5.2 Relative atomic mass

It is important to realise that the atomic mass of isotopes of the same element will be different because they have a different number of nucleons. Chlorine, for example, has two common isotopes which are chlorine-35 and chlorine-37. Chlorine-35 has an atomic mass of 35 u, while chlorine-37 has an atomic mass of 37 u. In the world around us, both of these isotopes occur naturally. It doesn't make sense to say that the element chlorine has an atomic mass of 35 u, or that it has an atomic mass of 37 u. Neither of these are absolutely true since the mass varies depending on the form in which the element occurs. We need to look at how much more common one is than the other in order to calculate the **relative atomic mass** for the element chlorine. This is then the number that will appear on the Periodic Table.



Definition: Relative atomic mass

Relative atomic mass is the average mass of one atom of all the naturally occurring isotopes of a particular chemical element, expressed in atomic mass units.



Worked Example 4: The relative atomic mass of an isotopic element

Question: The element chlorine has two isotopes, chlorine-35 and chlorine-37. The abundance of these isotopes when they occur naturally is 75% chlorine-35 and 25% chlorine-37. Calculate the *average* relative atomic mass for chlorine.

Answer

Step 1 : Calculate the mass contribution of chlorine-35 to the average relative atomic mass

Contribution of CI-35 = $(75/100 \times 35) = 26.25 \text{ u}$

Step 2 : Calculate the contribution of chlorine-37 to the average relative atomic mass

Contribution of Cl-37 = $(25/100 \times 37) = 9.25 \text{ u}$

Step 3 : Add the two values to arrive at the average relative atomic mass of chlorine

Relative atomic mass of chlorine = 26.25 u + 9.25 u = 35.5 u.

If you look on the periodic table, the average relative atomic mass for chlorine is 35,5 u. You will notice that for many elements, the relative atomic mass that is shown is not a whole number. You should now understand that this number is the *average* relative atomic mass for those elements that have naturally occurring isotopes.



Exercise: Isotopes

You are given a sample that contains carbon-12 and carbon-14.

1. Complete the table below:

Isotope	Z	Α	Protons	Neutrons	Electrons
Carbon-12					
Carbon-14					
Chlorine-35					
Chlorine-37					

2. If the sample you have contains 90% carbon-12 and 10% carbon-14, calculate the relative atomic mass of an atom in that sample.

Activity :: Group Discussion : The changing nature of scientific knowledge Scientific knowledge is not static: it changes and evolves over time as scientists build on the ideas of others to come up with revised (and often improved) theories and ideas. In this chapter for example, we saw how peoples' understanding of atomic structure changed as more information was gathered about the atom. There are many more examples like this one in the field of science. Think for example, about our knowledge of the solar system and the origin of the universe, or about the particle and wave nature of light.

Often, these changes in scientific thinking can be very controversial because they disturb what people have come to know and accept. It is important that we realise that what we know *now* about science may also change. An important part of being a scientist is to be a *critical thinker*. This means that you need to question information that you are given and decide whether it is accurate and whether it can be accepted as true. At the same time, you need to learn to be open to new ideas and not to become stuck in what you believe is right... there might just be something new waiting around the corner that you have not thought about!

In groups of 4-5, discuss the following questions:

- Think about some other examples where scientific knowledge has changed because of new ideas and discoveries:
 - What were these new ideas?
 - Were they controversial? If so, why?
 - What role (if any) did *technology* play in developing these new ideas?
 - How have these ideas affected the way we understand the world?
- Many people come up with their own ideas about how the world works. The same is true in science. So how do we, and other scientists, know what to believe and what not to? How do we know when new ideas are 'good' science or 'bad' science? In your groups, discuss some of the things that would need to be done to check whether a new idea or theory was worth listening to, or whether it was not.
- Present your ideas to the rest of the class.

3.6 Energy quantisation and electron configuration

3.6.1 The energy of electrons

You will remember from our earlier discussions, that an atom is made up of a central nucleus, which contains protons and neutrons, and that this nucleus is surrounded by electrons. Although

^{3.} In another sample, you have 22.5% Cl-37 and 77.5% Cl-35. Calculate the relative atomic mass of an atom in that sample.

these electrons all have the same charge and the same mass, each electron in an atom has a different amount of *energy*. Electrons that have the *lowest* energy are found closest to the nucleus where the attractive force of the positively charged nucleus is the greatest. Those electrons that have *higher* energy, and which are able to overcome the attractive force of the nucleus, are found further away.

3.6.2 Energy quantisation and line emission spectra

If the energy of an atom is increased (for example when a substance is heated), the energy of the electrons inside the atom can be increased (when an electron has a higher energy than normal it is said to be "excited"). For the excited electron to go back to its original energy (called the ground state), it needs to release energy. It releases energy by emitting light. If one heats up different elements, one will see that for each element, light is emitted only at certain frequencies (or wavelengths). Instead of a smooth continuum of frequencies, we see lines (called emission lines) at particular frequencies. These frequencies correspond to the energy of the emitted light. If electrons could be excited to any energy and lose any amount of energy, there would be a continuous spread of light frequencies emitted. However, the sharp lines we see mean that there are only certain particular energies that an electron can be excited to, or can lose, for each element.

You can think of this like going up a flight of steps: you can't lift your foot by *any* amount to go from the ground to the first step. If you lift your foot too low you'll bump into the step and be stuck on the ground level. You have to lift your foot just the right amount (the height of the step) to go to the next step, and so on. The same goes for electrons and the amount of energy they can have. This is called **quantisation of energy** because there are only certain quantities of energy that an electron can have in an atom. Like steps, we can think of these quantities as **energy levels** in the atom. The energy of the light released when an electron drops down from a higher energy level to a lower energy level is the same as the difference in energy between the two levels.

3.6.3 Electron configuration

Electrons are arranged in energy levels around the nucleus of an atom. Electrons that are in the energy level that is closest to the nucleus, will have the lowest energy and those further away will have a higher energy. Each energy level can only hold a certain number of electrons, and an electron will only be found in the second energy level once the first energy level is full. The same rule applies for the higher energy levels. You will need to learn the following rules:

- The 1st energy level can hold a maximum of 2 electrons
- The 2nd energy level can hold a maximum of 8 electrons
- The 3rd energy level can hold a maximum of 8 electrons
- If the number of electrons in the atom is greater than 18, they will need to move to the 4th energy level.

In the following examples, the energy levels are shown as concentric circles around the central nucleus.

1. Lithium

Lithium (Li) has an atomic number of 3, meaning that in a neutral atom, the number of electrons will also be 3. The first two electrons are found in the first energy level, while the third electron is found in the second energy level (figure 3.11).

2. Fluorine

Fluorine (F) has an atomic number of 9, meaning that a neutral atom also has 9 electrons. The first 2 electrons are found in the first energy level, while the other 7 are found in the second energy level (figure 3.12).



Figure 3.4: The arrangement of electrons in a lithium atom.



Figure 3.5: The arrangement of electrons in a fluorine atom.

3. Argon

Argon has an atomic number of 18, meaning that a neutral atom also has 18 electrons. The first 2 electrons are found in the first energy level, the next 8 are found in the second energy level, and the last 8 are found in the third energy level (figure 3.6).



Figure 3.6: The arrangement of electrons in an argon atom.

But the situation is slightly more complicated than this. Within each energy level, the electrons move in **orbitals**. An orbital defines the spaces or regions where electrons move.



Definition: Atomic orbital

An atomic orbital is the region in which an electron may be found around a single atom.

There are different orbital shapes, but we will be dealing with only two. These are the 's' and 'p' orbitals (there are also 'd' and 'f' orbitals). The first energy level contains only one 's' orbital, the second energy level contains one 's' orbital and three 'p' orbitals and the third energy level also contains one 's' orbital and three 'p' orbitals. Within each energy level, the 's' orbital is at a lower energy than the 'p' orbitals. This arrangement is shown in figure 3.7.

When we want to show how electrons are arranged in an atom, we need to remember the following principles:

3.6



Figure 3.7: The positions of the first ten orbits of an atom on an energy diagram. Note that each block is able to hold two electrons.

- Each orbital can only hold **two electrons**. Electrons that occur together in an orbital are called an **electron pair**. These electrons spin in opposite directions around their own axes.
- An electron will always try to enter an orbital with the lowest possible energy.
- An electron will occupy an orbital on its own, rather than share an orbital with another electron. An electron would also rather occupy a lower energy orbital *with* another electron, before occupying a higher energy orbital. In other words, within one energy level, electrons will fill an 's' orbital before starting to fill 'p' orbitals.

The way that electrons are arranged in an atom is called its electron configuration.



Definition: Electron configuration

Electron configuration is the arrangement of electrons in an atom, molecule, or other physical structure.

An element's electron configuration can be represented using **Aufbau diagrams** or energy level diagrams. An Aufbau diagram uses arrows to represent electrons. You can use the following steps to help you to draw an Aufbau diagram:

- 1. Determine the number of electrons that the atom has.
- 2. Fill the 's' orbital in the first energy level (the 1s orbital) with the first two electrons.
- 3. Fill the 's' orbital in the second energy level (the 2s orbital) with the second two electrons.
- 4. Put one electron in each of the three 'p' orbitals in the second energy level (the 2p orbitals), and then if there are still electrons remaining, go back and place a second electron in each of the 2p orbitals to complete the electron pairs.
- 5. Carry on in this way through each of the successive energy levels until all the electrons have been drawn.



Important:

When there are two electrons in an orbital, the electrons are called an **electron pair**. If the orbital only has one electron, this electron is said to be an **unpaired electron**. Electron pairs are shown with arrows in opposite directions. This is because when two electrons occupy the same orbital, they spin in opposite directions on their axes.

An Aufbau diagram for the element Lithium is shown in figure 3.8.



Figure 3.8: The electron configuration of Lithium, shown on an Aufbau diagram

A special type of notation is used to show an atom's electron configuration. The notation describes the energy levels, orbitals and the number of electrons in each. For example, the electron configuration of lithium is $1s^2 2s^1$. The number and letter describe the energy level and orbital, and the number above the orbital shows how many electrons are in that orbital.

Aufbau diagrams for the elements fluorine and argon are shown in figures 3.9 and 3.10 respectively. Using standard notation, the electron configuration of fluorine is $1s^2 2s^2 2p^5$ and the electron configuration of argon is $1s^2 2s^2 2p^6 3s^2 3p^6$.



3.6

Figure 3.9: An Aufbau diagram showing the electron configuration of fluorine

3.6.4 Core and valence electrons

Electrons in the outermost energy level of an atom are called **valence electrons**. The electrons that are in the energy shells closer to the nucleus are called **core electrons**. Core electrons are all the electrons in an atom, excluding the valence electrons. An element that has its valence energy level full is *more stable* and *less likely to react* than other elements with a valence energy level that is not full.



Definition: Valence electrons The electrons in the outer energy level of an atom



Definition: Core electrons All the electrons in an atom, excluding the valence electrons

3.6.5 The importance of understanding electron configuration

By this stage, you may well be wondering why it is important for you to understand how electrons are arranged around the nucleus of an atom. Remember that during chemical reactions, when atoms come into contact with one another, it is the *electrons* of these atoms that will interact first. More specifically, it is the **valence electrons** of the atoms that will determine how they



Figure 3.10: An Aufbau diagram showing the electron configuration of argon

react with one another.

3.6

To take this a step further, an atom is at its most stable (and therefore *unreactive*) when all its orbitals are full. On the other hand, an atom is least stable (and therefore most *reactive*) when its valence electron orbitals are not full. This will make more sense when we go on to look at chemical bonding in a later chapter. To put it simply, the valence electrons are largely responsible for an element's chemical behaviour, and elements that have the same number of valence electrons often have similar chemical properties.

Exercise: Energy diagrams and electrons

- 1. Draw Aufbau diagrams to show the electron configuration of each of the following elements:
 - (a) magnesium
 - (b) potassium
 - (c) sulfur
 - (d) neon
 - (e) nitrogen
- 2. Use the Aufbau diagrams you drew to help you complete the following table:

Element	No. o	of	No.	of	No.	of	Electron
	energy		core	elec-	valen	се	config-
	levels		trons		elect	rons	uration
							(standard
							notation)
Mg							
K							
S							
Ne							
N							

3. Rank the elements used above in order of *increasing reactivity*. Give reasons for the order you give.

Activity :: Group work : Building a model of an atom

Earlier in this chapter, we talked about different 'models' of the atom. In science, one of the uses of models is that they can help us to understand the structure of something that we can't see. In the case of the atom, models help us to build a picture in our heads of what the atom looks like.

Models are often simplified. The small toy cars that you may have played with as a child are models. They give you a good idea of what a real car looks like, but they are much smaller and much simpler. A model cannot always be absolutely accurate and it is important that we realise this so that we don't build up a false idea about something.

In groups of 4-5, you are going to build a model of an atom. Before you start, think about these questions:

- What information do I know about the structure of the atom? (e.g. what parts make it up? how big is it?)
- What materials can I use to represent these parts of the atom as accurately as I can?
- How will I put all these different parts together in my model?

As a group, share your ideas and then plan how you will build your model. Once you have built your model, discuss the following questions:

- Does our model give a good idea of what the atom actually looks like?
- In what ways is our model *inaccurate*? For example, we know that electrons *move* around the atom's nucleus, but in your model, it might not have been possible for you to show this.
- Are there any ways in which our model could be improved?

Now look at what other groups have done. Discuss the same questions for each of the models you see and record your answers.

3.7 Ionisation Energy and the Periodic Table

3.7.1 lons

In the previous section, we focused our attention on the electron configuration of *neutral* atoms. In a neutral atom, the number of protons is the same as the number of electrons. But what

happens if an atom *gains* or *loses* electrons? Does it mean that the atom will still be part of the same element?

A change in the number of electrons of an atom does not change the type of atom that it is. However, the *charge* of the atom will change. If electrons are added, then the atom will become *more negative*. If electrons are taken away, then the atom will become *more positive*. The atom that is formed in either of these cases is called an **ion**. Put simply, an ion is a charged atom.



Definition: Ion

An ion is a charged atom. A positively charged ion is called a **cation** e.g. Na^+ , and a negatively charged ion is called an **anion** e.g. F^- . The charge on an ion depends on the number of electrons that have been lost or gained.

Look at the following examples. Notice the number of valence electrons in the neutral atom, the number of electrons that are lost or gained, and the final charge of the ion that is formed.

Lithium

A lithium atoms loses one electrons to form a positive ion (figure 3.11).



Li atom with 3 electrons

Li⁺ ion with only 2 electrons

Figure 3.11: The arrangement of electrons in a lithium ion.

In this example, the lithium atom loses an electron to form the cation Li⁺.

Fluorine

A fluorine atom gains one electron to form a negative ion (figure 3.12).



Figure 3.12: The arrangement of electrons in a fluorine ion.

- 1. Use the diagram for lithium as a guide and draw similar diagrams to show how each of the following ions is formed:
 - (a) Mg^{2+}
 - (b) Na⁺
 - (c) Cl⁻
 - (d) O²⁻
- 2. Do you notice anything interesting about the charge on each of these ions? Hint: Look at the number of valence electrons in the neutral atom and the charge on the final ion.

Observations:

Once you have completed the activity, you should notice that:

- In each case the number of electrons that is either gained or lost, is the same as the number of electrons that are needed for the atoms to achieve a full or an empty valence energy level.
- If you look at an energy level diagram for sodium (Na), you will see that in a neutral atom, there is only one valence electron. In order to achieve an empty valence level, and therefore a more stable state for the atom, this electron will be *lost*.
- In the case of oxygen (O), there are six valence electrons. To fill the valence energy level, it makes more sense for this atom to *gain* two electrons. A negative ion is formed.

3.7.2 Ionisation Energy

lonisation energy is the energy that is needed to remove one electron from an atom. The ionisation energy will be different for different atoms.

The second ionisation energy is the energy that is needed to remove a second electron from an atom, and so on. As an energy level becomes more full, it becomes more and more difficult to remove an electron and the ionisation energy *increases*. On the Periodic Table of the Elements, a *group* is a vertical column of the elements, and a *period* is a horizontal row. In the periodic table, ionisation energy *increases* across a period, but *decreases* as you move down a group. The lower the ionisation energy, the more reactive the element will be because there is a greater chance of electrons being involved in chemical reactions. We will look at this in more detail in the next section.

Exercise: The formation of ions Match the information in column A with the information in column B by writing only the letter (A to I) next to the question number (1 to 7)

1. A positive ion that has 3 less electrons	A. Mg^{2+}
than its neutral atom	
2. An ion that has 1 more electron than	B. CI-
its neutral atom	
3. The anion that is formed when	C. CO_3^{2-}
bromine gains an electron	-
4. The cation that is formed from a mag-	D. Al ³⁺
nesium atom	
5. An example of a compound ion	E. Br ^{2–}
6. A positive ion with the electron con-	F. K ⁺
figuration of argon	
7. A negative ion with the electron con-	G. Mg ⁺
figuration of neon	
	H. O ^{2–}
	I. Br [_]

3.8 The Arrangement of Atoms in the Periodic Table

The **periodic table of the elements** is a tabular method of showing the chemical elements. Most of the work that was done to arrive at the periodic table that we know, can be attributed to a man called **Dmitri Mendeleev** in 1869. Mendeleev was a Russian chemist who designed the table in such a way that recurring ("periodic") trends in the properties of the elements could be shown. Using the trends he observed, he even left gaps for those elements that he thought were 'missing'. He even predicted the properties that he thought the missing elements would have when they were discovered. Many of these elements were indeed discovered and Mendeleev's predictions were proved to be correct.

To show the recurring properties that he had observed, Mendeleev began new rows in his table so that elements with similar properties were in the same vertical columns, called **groups**. Each row was referred to as a **period**. One important feature to note in the periodic table is that all the non-metals are to the right of the zig-zag line drawn under the element boron. The rest of the elements are metals, with the exception of hydrogen which occurs in the first block of the table despite being a non-metal.



Figure 3.13: A simplified diagram showing part of the Periodic Table

3.8.1 Groups in the periodic table

A group is a vertical column in the periodic table, and is considered to be the most important way of classifying the elements. If you look at a periodic table, you will see the groups numbered

at the top of each column. The groups are numbered from left to right as follows: 1, 2, then an open space which contains the **transition elements**, followed by groups 3 to 8. These numbers are normally represented using roman numerals. In some periodic tables, all the groups are numbered from left to right from number 1 to number 18. In some groups, the elements display very similar chemical properties, and the groups are even given separate names to identify them.

The characteristics of each group are mostly determined by the electron configuration of the atoms of the element.

• Group 1: These elements are known as the alkali metals and they are very reactive.



Figure 3.14: Electron diagrams for some of the Group 1 elements

Activity :: Investigation : The properties of elements Refer to figure 3.14.

- 1. Use a Periodic Table to help you to complete the last two diagrams for sodium (Na) and potassium (K).
- 2. What do you notice about the number of electrons in the valence energy level in each case?
- 3. Explain why elements from group 1 are more reactive than elements from group 2 on the periodic table (Hint: Think back to 'ionisation energy').
- *Group 2:* These elements are known as the **alkali earth metals**. Each element only has two valence electrons and so in chemical reactions, the group 2 elements tend to *lose* these electrons so that the energy shells are complete. These elements are less reactive than those in group 1 because it is more difficult to lose two electrons than it is to lose one. *Group 3* elements have three valence electrons.



Important: The number of valence electrons of an element corresponds to its group number on the periodic table.

- *Group 7:* These elements are known as the **halogens**. Each element is missing just one electron from its outer energy shell. These elements tend to *gain* electrons to fill this shell, rather than losing them.
- *Group 8:* These elements are the **noble gases**. All of the energy shells of the halogens are full, and so these elements are very unreactive.
- *Transition metals:* The differences between groups in the transition metals are not usually dramatic.



Figure 3.15: Electron diagrams for two of the noble gases, helium (He) and neon (Ne).

It is worth noting that in each of the groups described above, the **atomic diameter** of the elements increases as you move down the group. This is because, while the number of valence electrons is the same in each element, the number of core electrons increases as one moves down the group.

3.8.2 Periods in the periodic table

A **period** is a horizontal row in the periodic table of the elements. Some of the trends that can be observed within a period are highlighted below:

- As you move from one group to the next within a period, the number of valence electrons increases by one each time.
- Within a single period, all the valence electrons occur in the same energy shell. If the period increases, so does the energy shell in which the valence electrons occur.
- In general, the diameter of atoms decreases as one moves from left to right across a period. Consider the attractive force between the positively charged nucleus and the negatively charged electrons in an atom. As you move across a period, the number of protons in each atom increases. The number of electrons also increases, but these electrons will still be in the same energy shell. As the number of protons increases, the force of attraction between the nucleus and the electrons will increase and the atomic diameter will decrease.
- Ionisation energy increases as one moves from left to right across a period. As the valence
 electron shell moves closer to being full, it becomes more difficult to remove electrons. The
 opposite is true when you move down a *group* in the table because more energy shells are
 being added. The electrons that are closer to the nucleus 'shield' the outer electrons from
 the attractive force of the positive nucleus. Because these electrons are not being held
 to the nucleus as strongly, it is easier for them to be removed and the ionisation energy
 decreases.
- In general, the reactivity of the elements decreases from left to right across a period.

Exercise: Trends in ionisation energy

Refer to the data table below which gives the ionisation energy (in kJ/mol) and atomic number (Z) for a number of elements in the periodic table:
Ζ	Ionisation energy	Ζ	Ionisation energy
1	1310	10	2072
2	2360	11	494
3	517	12	734
4	895	13	575
5	797	14	783
6	1087	15	1051
7	1397	16	994
8	1307	17	1250
9	1673	18	1540

- 1. Draw a line graph to show the relationship between atomic number (on the x-axis) and ionisation energy (y-axis).
- 2. Describe any trends that you observe.

3. Explain why...

- (a) the ionisation energy for Z=2 is higher than for Z=1
- (b) the ionisation energy for Z=3 is lower than for Z=2
- (c) the ionisation energy increases between Z=5 and Z=7

Exercise: Elements in the Periodic Table

Refer to the elements listed below:

Lithium (Li); Chlorine (Cl); Magnesium (Mg); Neon (Ne); Oxygen (O); Calcium (Ca); Carbon (C)

Which of the elements listed above:

- 1. belongs to Group 1
- 2. is a halogen
- 3. is a noble gas
- 4. is an alkali metal
- 5. has an atomic number of 12
- 6. has 4 neutrons in the nucleus of its atoms
- 7. contains electrons in the 4th energy level
- 8. has only one valence electron
- 9. has all its energy orbitals full
- 10. will have chemical properties that are most similar
- 11. will form positive ions

3.9 Summary

 Much of what we know today about the atom, has been the result of the work of a number of scientists who have added to each other's work to give us a good understanding of atomic structure.

- Some of the important scientific contributors include J.J.Thomson (discovery of the electron, which led to the Plum Pudding Model of the atom), Ernest Rutherford (discovery that positive charge is concentrated in the centre of the atom) and Niels Bohr (the arrangement of electrons around the nucleus in energy levels).
- Because of the very small mass of atoms, their mass in measured in atomic mass units (u). 1 u = 1.67×10^{-24} g.
- An atom is made up of a central nucleus (containing protons and neutrons), surrounded by electrons.
- The atomic number (Z) is the number of protons in an atom.
- The atomic mass number (A) is the number of protons and neutrons in the nucleus of an atom.
- The **standard notation** that is used to write an element, is ${}^{A}_{Z}X$, where X is the element symbol, A is the atomic mass number and Z is the atomic number.
- The **isotope** of a particular element is made up of atoms which have the same number of protons as the atoms in the original element, but a different number of neutrons. This means that not all atoms of an element will have the same atomic mass.
- The **relative atomic mass** of an element is the average mass of one atom of all the naturally occurring isotopes of a particular chemical element, expressed in atomic mass units. The relative atomic mass is written under the elements' symbol on the Periodic Table.
- The energy of electrons in an atom is quantised. Electrons occur in specific energy levels around an atom's nucleus.
- Within each energy level, an electron may move within a particular shape of **orbital**. An orbital defines the space in which an electron is most likely to be found. There are different orbital shapes, including s, p, d and f orbitals.
- Energy diagrams such as Aufbau diagrams are used to show the electron configuration of atoms.
- The electrons in the outermost energy level are called valence electrons.
- The electrons that are not valence electrons are called core electrons.
- Atoms whose outermost energy level is full, are less chemically reactive and therefore more stable, than those atoms whose outer energy level is not full.
- An ion is a charged atom. A cation is a positively charged ion and an anion is a negatively charged ion.
- When forming an ion, an atom will lose or gain the number of electrons that will make its
 valence energy level full.
- An element's ionisation energy is the energy that is needed to remove one electron from an atom.
- Ionisation energy increases across a **period** in the Periodic Table.
- Ionisation energy decreases down a group in the Periodic Table.

Exercise: Summary

- 1. Write down only the word/term for each of the following descriptions.
 - (a) The sum of the number of protons and neutrons in an atom

- (b) The defined space around an atom's nucleus, where an electron is most likely to be found
- 2. For each of the following, say whether the statement is True or False. If it is False, re-write the statement correctly.
 - (a) $^{20}_{10}$ Ne and $^{22}_{10}$ Ne each have 10 protons, 12 electrons and 12 neutrons.
 - (b) The atomic mass of any atom of a particular element is always the same.
 - (c) It is safer to use helium gas rather than hydrogen gas in balloons.
 - (d) Group 1 elements readily form negative ions.
- 3. Multiple choice questions: In each of the following, choose the **one** correct answer.
 - (a) The three basic components of an atom are:
 - i. protons, neutrons, and ions
 - ii. protons, neutrons, and electrons
 - iii. protons, neutrinos, and ions
 - iv. protium, deuterium, and tritium
 - (b) The charge of an atom is...
 - i. positive
 - ii. neutral
 - iii. negative
 - (c) If Rutherford had used neutrons instead of alpha particles in his scattering experiment, the neutrons would...
 - i. not deflect because they have no charge
 - ii. have deflected more often
 - iii. have been attracted to the nucleus easily
 - iv. have given the same results
 - (d) Consider the isotope $\frac{234}{92}$ U. Which of the following statements is *true*?
 - i. The element is an isotope of $^{234}_{94}$ Pu
 - ii. The element contains 234 neutrons
 - iii. The element has the same electron configuration as $^{238}_{92}$ U
 - iv. The element has an atomic mass number of 92
 - (e) The electron configuration of an atom of chlorine can be represented using the following notation:
 - i. 1s² 2s⁸ 3s⁷
 - ii. 1s² 2s² 2p⁶ 3s² 3p⁵
 - iii. 1s² 2s² 2p⁶ 3s² 3p⁶
 - iv. $1s^2 2s^2 2p^5$
- 4. The following table shows the first ionisation energies for the elements of period 1 and 2.

Period	Element	First ionisation energy $(kJ.mol^{-1})$
1	Н	1312
	He	2372
	Li	520
	Be	899
	В	801
	С	1086
2	Ν	1402
	0	1314
	F	1681
	Ne	2081

- (a) What is the meaning of the term *first ionisation energy*?
- (b) Identify the pattern of first ionisation energies in a period.
- (c) Which TWO elements exert the strongest attractive forces on their electrons? Use the data in the table to give a reason for your answer.

- (d) Draw Aufbau diagrams for the TWO elements you listed in the previous question and explain why these elements are so stable.
- (e) It is safer to use helium gas than hydrogen gas in balloons. Which property of helium makes it a safer option?
- (f) 'Group 1 elements readily form positive ions'. Is this statement correct? Explain your answer by referring to the table.

Chapter 4

Atomic Combinations - Grade 11

When you look at the matter around you, you will realise that atoms seldom exist on their own. More often, the things around us are made up of different atoms that have been joined together. This is called **chemical bonding**. Chemical bonding is one of the most important processes in chemistry because it allows all sorts of different molecules and combinations of atoms to form, which then make up the objects in the complex world around us. There are, however, some atoms that *do* exist on their own, and which do not bond with others. The **noble gases** in Group 8 of the Periodic Table, behave in this way. They include elements like neon (Ne), helium (He) and argon (Ar). The important question then is, why do some atoms bond but others do not?

4.1 Why do atoms bond?

As we begin this section, it's important to remember that what we will go on to discuss is a *model* of bonding, that is based on a particular *model* of the atom. You will remember from section 3.1 that a model is a *representation* of what is happening in reality. In the model of the atom that has been used so far, the atom is made up of a central nucleus, surrounded by electrons that are arranged in fixed energy levels (also sometimes called *shells*). Within each energy level, electrons move in *orbitals* of different shapes. The electrons in the outermost energy level of an atom are called the **valence electrons**. This model of the atom is useful in trying to understand how different types of bonding take place between atoms.

You will remember from these earlier discussions of electrons and energy levels in the atom, that electrons always try to occupy the *lowest* possible energy level. In the same way, an atom also prefers to exist at the lowest possible energy state so that it is most *stable*. An atom is most stable when all its valence electron orbitals are *full*. In other words, the outer energy level of the atom contains the maximum number of electrons that it can. A stable atom is also an *unreactive* one, and is unlikely to bond with other atoms. This explains why the noble gases are unreactive and why they exist as atoms, rather than as molecules. Look for example at the electron configuration of neon $(1s^2 2s^2 3p^6)$. Neon has eight valence electrons in its valence energy shell. This is the maximum that it can hold and so neon is very stable and unreactive, and will not form new bonds. Other atoms, whose valence energy levels are not full, are more likely to bond in order to become more stable. We are going to look a bit more closely at some of the energy changes that take place when atoms bond.

4.2 Energy and bonding

Let's start by imagining that there are two hydrogen atoms approaching one another. As they move closer together, there are three forces that act on the atoms at the same time. These forces are shown in figure 4.1 and are described below:



Figure 4.1: Forces acting on two approaching atoms: (1) repulsion between electrons, (2) attraction between protons and electrons and (3) repulsion between protons.

- 1. repulsive force between the electrons of the atoms, since like charges repel
- 2. attractive force between the nucleus of one atom and the electrons of another
- 3. repulsive force between the two positively-charged nuclei

Now look at figure 4.2 to understand the energy changes that take place when the two atoms move towards each other.



Figure 4.2: Graph showing the change in energy that takes place as atoms move closer together

In the example of the two hydrogen atoms, where the resultant force between them is attraction, the energy of the system is zero when the atoms are far apart (point A), because there is no interaction between the atoms. When the atoms are closer together, attractive forces dominate and the atoms are pulled towards each other. As this happens, the *potential energy* of the system decreases because energy would now need to be *supplied* to the system in order to move the atoms apart. However, as the atoms move closer together (i.e. *left* along the horizontal axis of the graph), repulsive forces start to dominate and this causes the potential energy of the system to rise again. At some point, the attractive and repulsive effects are balanced, and the energy of the system is at its minimum (point X). It is at this point, when the energy is at a minimum, that bonding takes place.

The distance marked 'P' is the **bond length**, i.e. the distance between the nuclei of the atoms when they bond. 'Q' represents the **bond energy** i.e. the amount of energy that must be added to the system to break the bonds that have formed. **Bond strength** means how strongly one atom attracts and is held to another. The strength of a bond is related to the bond length, the size of the bonded atoms and the number of bonds between the atoms. In general, the shorter the bond length, the stronger the bond between the atoms, and the smaller the atoms involved, the stronger the bond. The greater the number of bonds between atoms, the greater will be the bond strength.

4.3 What happens when atoms bond?

A **chemical bond** is formed when atoms are held together by attractive forces. This attraction occurs when electrons are *shared* between atoms, or when electrons are *exchanged* between the atoms that are involved in the bond. The sharing or exchange of electrons takes place so that the outer energy levels of the atoms involved are filled and the atoms are more stable. If an electron is **shared**, it means that it will spend its time moving in the electron orbitals around *both* atoms. If an electron is **exchanged** it means that it is transferred from one atom to another, in other words one atom *gains* an electron while the other *loses* an electron.



Definition: Chemical bond

A chemical bond is the physical process that causes atoms and molecules to be attracted to each other, and held together in more stable chemical compounds.

The type of bond that is formed depends on the elements that are involved. In this section, we will be looking at three types of chemical bonding: **covalent**, **ionic** and **metallic bonding**.

You need to remember that it is the *valence electrons* that are involved in bonding and that atoms will try to fill their outer energy levels so that they are more stable.

4.4 Covalent Bonding

4.4.1 The nature of the covalent bond

Covalent bonding occurs between the atoms of **non-metals**. The outermost orbitals of the atoms overlap so that unpaired electrons in each of the bonding atoms can be shared. By overlapping orbitals, the outer energy shells of all the bonding atoms are filled. The shared electrons move in the orbitals around *both* atoms. As they move, there is an attraction between these negatively charged electrons and the positively charged nuclei, and this force holds the atoms together in a covalent bond.



Definition: Covalent bond

Covalent bonding is a form of chemical bonding where pairs of electrons are shared between atoms.

Below are a few examples. Remember that it is only the *valence electrons* that are involved in bonding, and so when diagrams are drawn to show what is happening during bonding, it is only these electrons that are shown. Circles and crosses represent electrons in different atoms.



Question: How do hydrogen and chlorine atoms bond covalently in a molecule of hydrogen chloride?

Answer

Step 1: Determine the electron configuration of each of the bonding atoms. A chlorine atom has 17 electrons, and an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^5$. A hydrogen atom has only 1 electron, and an electron configuration of $1s^1$.

Step 2 : Determine the number of valence electrons for each atom, and how many of the electrons are paired or unpaired.

Chlorine has 7 valence electrons. One of these electrons is unpaired. Hydrogen has 1 valence electron and it is unpaired.

Step 3 : Look to see how the electrons can be shared between the atoms so that the outermost energy levels of both atoms are full.

The hydrogen atom needs one more electron to complete its valence shell. The chlorine atom also needs one more electron to complete its shell. Therefore *one pair of electrons* must be shared between the two atoms. In other words, one electron from the chlorine atom will spend some of its time orbiting the hydrogen atom so that hydrogen's valence shell is full. The hydrogen electron will spend some of its time orbiting the chlorine atom so that chlorine's valence shell is also full. A molecule of hydrogen chloride is formed (figure 4.3). Notice the shared electron pair in the overlapping orbitals.





Figure 4.3: Covalent bonding in a molecule of hydrogen chloride



Worked Example 6: Covalent bonding involving multiple bonds

Question: How do nitrogen and hydrogen atoms bond to form a molecule of ammonia (NH_3) ?

Answer

Step 1 : Determine the electron configuration of each of the bonding atoms. A nitrogen atom has 7 electrons, and an electron configuration of $1s^2 2s^2 2p^3$. A hydrogen atom has only 1 electron, and an electron configuration of $1s^1$.

Step 2 : Determine the number of valence electrons for each atom, and how many of the electrons are paired or unpaired.

Nitrogen has 5 valence electrons meaning that 3 electrons are unpaired. Hydrogen has 1 valence electron and it is unpaired.

Step 3 : Look to see how the electrons can be shared between the atoms so that the outer energy shells of all atoms are full.

Each hydrogen atom needs one more electron to complete its valence energy shell. The nitrogen atom needs three more electrons to complete its valence energy shell. Therefore *three pairs of electrons* must be shared between the four atoms involved. The nitrogen atom will share three of its electrons so that each of the hydrogen atoms now has a complete valence shell. Each of the hydrogen atoms will share its electron with the nitrogen atom to complete its valence shell (figure 4.4).



The above examples all show **single covalent bonds**, where only one pair of electrons is shared between *the same two atoms*. If two pairs of electrons are shared between the same two atoms, this is called a **double bond**. A **triple bond** is formed if three pairs of electrons are shared.



P

Definition: Valency

The number of electrons in an atom which are used to form a bond.



Figure 4.5: A double covalent bond in an oxygen molecule

In the first example, the valency of both hydrogen and chlorine is one, therefore there is a single covalent bond between these two atoms. In the second example, nitrogen has a valency of three and hydrogen has a valency of one. This means that three hydrogen atoms will need to bond with a single nitrogen atom. There are three *single* covalent bonds in a molecule of ammonia. In the third example, the valency of oxygen is two. This means that each oxygen atom will form two bonds with another atom. Since there is only one other atom in a molecule of O_2 , a *double covalent* bond is formed between these two atoms.

Important: There is a relationship between the valency of an element and its position on the Periodic Table. For the elements in groups 1 to 4, the valency is the same as the group number. For elements in groups 5 to 7, the valency is calculated by subtracting the group number from 8. For example, the valency of fluorine (group 7) is 8-7=1, while the valency of calcium (group 2) is 2. Some elements have more than one possible valency, so you always need to be careful when you are writing a chemical formula. Often, the valency will be written in a bracket after the element symbol e.g. carbon (iv) oxide, means that in this molecule carbon has a valency of 4.

Exercise: Covalent bonding and valency

- 1. Explain the difference between the *valence electrons* and the *valency* of an element.
- 2. Complete the table below by filling in the number of valence electrons and the valency for each of the elements shown:

Element	No. of valence electrons	No. of elec- trons needed to fill outer shell	Valency
Mg			
К			
F			
Ar			
С			
N			
0			

- 3. Draw simple diagrams to show how electrons are arranged in the following covalent molecules:
 - (a) Calcium oxide (CaO)
 - (b) Water (H_2O)
 - (c) Chlorine (Cl₂)

4.5 Lewis notation and molecular structure

Although we have used diagrams to show the structure of molecules, there are other forms of notation that can be used, such as **Lewis notation** and **Couper notation**. **Lewis notation** uses dots and crosses to represent the **valence electrons** on different atoms. The chemical symbol of the element is used to represent the nucleus and the core electrons of the atom.

So, for example, a hydrogen atom would be represented like this:

```
Н•
```

A chlorine atom would look like this:

A molecule of hydrogen chloride would be shown like this:

$$\mathsf{H} \stackrel{\times \overset{\times}{\overset{}} \overset{\times}{\underset{\times} \overset{\times}{\overset{\times}}}}{\overset{\times}{\overset{\times}}}_{\overset{\times}{\overset{\times}}}$$

The dot and cross inbetween the two atoms, represent the pair of electrons that are shared in the covalent bond.



Worked Example 8: Lewis notation: Simple molecules

Question: Represent the molecule H_2O using Lewis notation

Answer

Step 1 : For each atom, determine the number of valence electrons in the atom, and represent these using dots and crosses.

The electron configuration of hydrogen is $1s^1$ and the electron configuration for oxygen is $1s^2$ $2s^2$ $2p^4$. Each hydrogen atom has one valence electron, which is unpaired, and the oxygen atom has six valence electrons with two unpaired.

$$2 \mathbf{H} \bullet \times \mathbf{O}_{\times}^{\times} \times \mathbf{O}_{\times}^{\times}$$

Step 2 : Arrange the electrons so that the outermost energy level of each atom is full.

The water molecule is represented below.



Worked Example 9: Lewis notation: Molecules with multiple bonds

Question: Represent the molecule HCN using Lewis notation

Answer

Step 1 : For each atom, determine the number of valence electrons that the atom has from its electron configuration.

The electron configuration of hydrogen is $1s^1$, the electron configuration of nitrogen is $1s^2 2s^2 2p^3$ and for carbon is $1s^2 2s^2 2p^2$. This means that hydrogen has one valence electron which is unpaired, carbon has four valence electrons, all of which are unpaired, and nitrogen has five valence electrons, three of which are unpaired.

$$\mathsf{H} \bullet \times \overset{\times}{\underset{\times}{\mathsf{C}}} \times \bullet \overset{\bullet \bullet}{\underset{\bullet}{\mathsf{N}}} \bullet$$

Step 2 : Arrange the electrons in the HCN molecule so that the outermost energy level in each atom is full.

The HCN molecule is represented below. Notice the three electron pairs between the nitrogen and carbon atom. Because these three covalent bonds are between the same two atoms, this is a *triple* bond.





Worked Example 10: Lewis notation: Atoms with variable valencies

Question: Represent the molecule H_2S using Lewis notation

Answer

Step 1 : Determine the number of valence electrons for each atom.

Hydrogen has an electron configuration of $1s^1$ and sulfur has an electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^4$. Each hydrogen atom has one valence electron which is unpaired, and sulfur has six valence electrons. Although sulfur has a variable valency, we know that the sulfur will be able to form 2 bonds with the hydrogen atoms. In this case, the valency of sulfur must be two.

$$2 \mathbf{H} \bullet \qquad \times \mathbf{S}_{\times}^{\times} \times \mathbf{S}_{\times}^{\times}$$

Step 2 : Arrange the atoms in the molecule so that the outermost energy level in each atom is full.

The H_2S molecule is represented below.



Another way of representing molecules is using **Couper notation**. In this case, only the electrons that are involved in the bond between the atoms are shown. A line is used for each covalent bond. Using Couper notation, a molecule of water and a molecule of HCN would be represented as shown in figures 4.6 and 4.7 below.

Figure 4.6: A water molecule represented using Couper notation

$$H - C \equiv N$$

Figure 4.7: A molecule of HCN represented using Couper notation

Extension: Dative covalent bonds

A **dative covalent bond** (also known as a coordinate covalent bond) is a description of covalent bonding between two atoms in which both electrons shared in the bond come from the same atom. This happens when a Lewis base (an electron donor) donates a pair of electrons to a Lewis acid (an electron acceptor). Lewis acids and bases will be discussed in section 15.1 in chapter 15.

One example of a molecule that contains a dative covalent bond is the ammonium ion (NH_4^+) shown in the figure below. The hydrogen ion H^+ does not contain any electrons, and therefore the electrons that are in the bond that forms between this ion and the nitrogen atom, come only from the nitrogen.



?

Exercise: Atomic bonding and Lewis notation

- 1. Represent each of the following *atoms* using Lewis notation:
 - (a) beryllium
 - (b) calcium
 - (c) lithium
- 2. Represent each of the following *molecules* using Lewis notation:
 - (a) bromine gas (Br₂)

(b) calcium chloride (CaCl₂)

(c) carbon dioxide (CO_2)

- 3. Which of the three molecules listed above contains a double bond?
- 4. Two chemical reactions are described below.
 - nitrogen and hydrogen react to form ammonia
 - carbon and hydrogen bond to form a molecule of methane (CH₄)

For each reaction, give:

- (a) the valency of each of the atoms involved in the reaction
- (b) the Lewis structure of the product that is formed
- (c) the chemical formula of the product
- (d) the name of the product
- 5. A chemical compound has the following Lewis notation:



- (a) How many valence electrons does element Y have?
- (b) What is the valency of element Y?
- (c) What is the valency of element X?
- (d) How many covalent bonds are in the molecule?
- (e) Suggest a name for the elements X and Y.

4.6 Electronegativity

Electronegativity is a measure of how strongly an atom pulls a shared electron pair towards it. The table below shows the electronegativities of a number of elements:

	Element	Electronegativity
	Hydrogen (H)	2.1
	Sodium (Na)	0.9
	Magnesium (Mg)	1.2
	Calcium (Ca)	1.0
ĺ	Chlorine (CI)	3.0
	Bromine (Br)	2.8

Table 4.1: Table of electronegativities for selected elements



Definition: Electronegativity

Electronegativity is a chemical property which describes the power of an atom to attract electrons towards itself.

The greater the electronegativity of an element, the stronger its attractive pull on electrons. For example, in a molecule of hydrogen bromide (HBr), the electronegativity of bromine (2.8) is higher than that of hydrogen (2.1), and so the shared electrons will spend more of their time closer to the bromine atom. Bromine will have a slightly negative charge, and hydrogen will have a slightly positive charge. In a molecule like hydrogen (H_2) where the electronegativities of the atoms in the molecule are the same, both atoms have a neutral charge.



The concept of electronegativity was introduced by *Linus Pauling* in 1932, and this became very useful in predicting the nature of bonds between atoms in molecules. In 1939, he published a book called 'The Nature of the Chemical Bond', which became one of the most influential chemistry books ever published. For this work, Pauling was awarded the Nobel Prize in Chemistry in 1954. He also received the Nobel Peace Prize in 1962 for his campaign against above-ground nuclear testing.

4.6.1 Non-polar and polar covalent bonds

Electronegativity can be used to explain the difference between two types of covalent bonds. **Non-polar covalent bonds** occur between two identical non-metal atoms, e.g. H_2 , Cl_2 and O_2 . Because the two atoms have the same electronegativity, the electron pair in the covalent bond is shared equally between them. However, if two different non-metal atoms bond then the shared electron pair will be pulled more strongly by the atom with the highest electronegativity. As a result, a **polar covalent bond** is formed where one atom will have a slightly negative charge and the other a slightly positive charge. This is represented using the symbols δ^+ (slightly positive) and δ^- (slightly negative). So, in a molecule such as hydrogen chloride (HCI), hydrogen is H^{δ^+} and chlorine is Cl^{δ^-} .

4.6.2 Polar molecules

Some molecules with polar covalent bonds are **polar molecules**, e.g. H_2O . But not *all* molecules with polar covalent bonds are polar. An example is CO_2 . Although CO_2 has two polar covalent bonds (between C⁺ atom and the two O⁻ atoms), the molecule itself is not polar. The reason is that CO_2 is a linear molecule and is therefore symmetrical. So there is no difference in charge between the two ends of the molecule. The *polarity* of molecules affects properties such as *solubility, melting points* and *boiling points*.

Definition: Polar and non-polar molecules

A **polar molecule** is one that has one end with a slightly positive charge, and one end with a slightly negative charge. A **non-polar molecule** is one where the charge is equally spread across the molecule.



Exercise: Electronegativity

- 1. In a molecule of hydrogen chloride (HCI),
 - (a) What is the electronegativity of hydrogen
 - (b) What is the electronegativity of chlorine?
 - (c) Which atom will have a slightly positive charge and which will have a slightly negative charge in the molecule?
 - (d) Is the bond a non-polar or polar covalent bond?
 - (e) Is the molecule polar or non-polar?

Molecule	Difference in electronegativity between atoms	Non-polar/polar covalent bond	Polar/non-polar molecule
H_2O			
HBr			
NO_2			
F_2			
CH_4			

2. Complete the table below:

4.7 Ionic Bonding

4.7.1 The nature of the ionic bond

You will remember that when atoms bond, electrons are either shared or they are transferred between the atoms that are bonding. In covalent bonding, electrons are shared between the atoms. There is another type of bonding, where electrons are transferred from one atom to another. This is called **ionic bonding**.

lonic bonding takes place when the difference in electronegativity between the two atoms is more than 1.7. This usually happens when a metal atom bonds with a non-metal atom. When the difference in electronegativity is large, one atom will attract the shared electron pair much more strongly than the other, causing electrons to be transferred from one atom to the other.



Definition: Ionic bond

An ionic bond is a type of chemical bond based on the electrostatic forces between two oppositely-charged ions. When ionic bonds form, a metal donates an electron, due to a low electronegativity, to form a positive ion or cation. The non-metal atom has a high electronegativity, and therefore readily gains electrons to form negative ions or anions. The two or more ions are then attracted to each other by electrostatic forces.

Example 1:

In the case of NaCl, the difference in electronegativity is 2.1. Sodium has only one valence electron, while chlorine has seven. Because the electronegativity of chlorine is higher than the electronegativity of sodium, chlorine will attract the valence electron in the sodium atom very strongly. This electron from sodium is transferred to chlorine. Sodium has lost an electron and forms a Na^+ ion. Chlorine gains an electron and forms a Cl^- ion. The attractive force between the positive and negative ion is what holds the molecule together.

The balanced equation for the reaction is:

$$Na + Cl \rightarrow NaCl$$

This can be represented using Lewis notation:

Example 2:

Another example of ionic bonding takes place between magnesium (Mg) and oxygen (O) to form magnesium oxide (MgO). Magnesium has two valence electrons and an electronegativity of 1.2, while oxygen has six valence electrons and an electronegativity of 3.5. Since oxygen has



Figure 4.8: Ionic bonding in sodium chloride

a higher electronegativity, it attracts the two valence electrons from the magnesium atom and these electrons are transferred from the magnesium atom to the oxygen atom. Magnesium loses two electrons to form Mg^{2+} , and oxygen gains two electrons to form O^{2-} . The attractive force between the oppositely charged ions is what holds the molecule together.

The balanced equation for the reaction is:

$$2Mg + O_2 \rightarrow 2MgO$$

Because oxygen is a diatomic molecule, two magnesium atoms will be needed to combine with two oxygen atoms to produce two molecules of magnesium oxide (MgO).



Figure 4.9: Ionic bonding in magnesium oxide

Important: Notice that the number of electrons that is either lost or gained by an atom during ionic bonding, is the same as the **valency** of that element



Exercise: Ionic compounds

- 1. Explain the difference between a *covalent* and an *ionic* bond.
- 2. Magnesium and chlorine react to form magnesium chloride.
 - (a) What is the difference in electronegativity between these two elements?
 - (b) Give the chemical formula for:
 - a magnesium ion
 - a choride ion
 - the ionic compound that is produced during this reaction
 - (c) Write a balanced chemical equation for the reaction that takes place.
- 3. Draw Lewis diagrams to represent the following ionic compounds:
 - (a) sodium iodide (Nal)
 - (b) calcium bromide (CaBr₂)
 - (c) potassium chloride (KCl)

4.7.2 The crystal lattice structure of ionic compounds

lonic substances are actually a combination of lots of ions bonded together into a giant molecule. The arrangement of ions in a regular, geometric structure is called a **crystal lattice**. So in fact NaCl does not contain one Na and one Cl ion, but rather a lot of these two ions arranged in a crystal lattice where the ratio of Na to Cl ions is 1:1. The structure of a crystal lattice is shown in figure 4.10.



Figure 4.10: The crystal lattice arrangement in an ionic compound (e.g. NaCl)

4.7.3 Properties of Ionic Compounds

lonic compounds have a number of properties:

- lons are arranged in a lattice structure
- Ionic solids are crystalline at room temperature
- The ionic bond is a strong electrical attraction. This means that ionic compounds are often hard and have high melting and boiling points
- lonic compounds are brittle, and bonds are broken along planes when the compound is stressed
- Solid crystals don't conduct electricity, but ionic solutions do

4.8 Metallic bonds

4.8.1 The nature of the metallic bond

The structure of a metallic bond is quite different from covalent and ionic bonds. In a metal bond, the valence electrons are *delocalised*, meaning that an atom's electrons do not stay around that one nucleus. In a metallic bond, the positive atomic nuclei (sometimes called the 'atomic kernels') are surrounded by a sea of delocalised electrons which are attracted to the nuclei (figure 4.11).



Definition: Metallic bond

Metallic bonding is the electrostatic attraction between the positively charged atomic nuclei of metal atoms and the delocalised electrons in the metal.



Figure 4.11: Positive atomic nuclei (+) surrounded by delocalised electrons (\bullet)

4.8.2 The properties of metals

Metals have several unique properties as a result of this arrangement:

• Thermal conductors

Metals are good conductors of heat and are therefore used in cooking utensils such as pots and pans. Because the electrons are loosely bound and are able to move, they can transport heat energy from one part of the material to another.

• Electrical conductors

Metals are good conductors of electricity, and are therefore used in electrical conducting wires. The loosely bound electrons are able to move easily and to transfer charge from one part of the material to another.

• Shiny metallic lustre

Metals have a characteristic shiny appearance and are often used to make jewellery. The loosely bound electrons are able to absorb and reflect light at all frequencies, making metals look polished and shiny.

• Malleable and ductile

This means that they can be bent into shape without breaking (malleable) and can be stretched into thin wires (ductile) such as copper, which can then be used to conduct electricity. Because the bonds are not fixed in a particular direction, atoms can slide easily over one another, making metals easy to shape, mould or draw into threads.

Melting point

Metals usually have a high melting point and can therefore be used to make cooking pots and other equipment that needs to become very hot, without being damaged. The high melting point is due to the high strength of metallic bonds.

• Density

Metals have a high density because their atoms are packed closely together.



Exercise: Chemical bonding

- 1. Give two examples of everyday objects that contain..
 - (a) covalent bonds
 - (b) ionic bonds

- (c) metallic bonds
- 2. Complete the table which compares the different types of bonding:

	Covalent	lonic	Metallic
Types of atoms involved			
Nature of bond between atoms			
Melting Point (high/low)			
Conducts electricity? (yes/no)			
Other properties			

3. Complete the table below by identifying the type of bond (covalent, ionic or metallic) in each of the compounds:

Molecular formula	Type of bond
H_2SO_4	
FeS	
Nal	
$MgCl_2$	
Zn	

- 4. Which of these substances will conduct electricity most effectively? Give a reason for your answer.
- 5. Use your knowledge of the different types of bonding to explain the following statements:
 - (a) Swimming during an electric thunderstorm (i.e. where there is lightning) can be very dangerous.
 - (b) Most jewellery items are made from metals.
 - (c) Plastics are good insulators.

4.9 Writing chemical formulae

4.9.1 The formulae of covalent compounds

To work out the formulae of covalent compounds, we need to use the valency of the atoms in the compound. This is because the valency tells us how many bonds each atom can form. This in turn can help to work out how many atoms of each element are in the compound, and therefore what its formula is. The following are some examples where this information is used to write the chemical formula of a compound.



Worked Example 11: Formulae of covalent compounds

Question: Write the chemical formula for water

Answer

Step 1 : Write down the elements that make up the compound.

A molecule of water contains the elements hydrogen and oxygen.

Step 2 : Determine the valency of each element

The valency of hydrogen is 1 and the valency of oxygen is 2. This means that oxygen can form two bonds with other elements and each of the hydrogen atoms can form one.

Step 3 : Write the chemical formula

Using the valencies of hydrogen and oxygen, we know that in a single water molecule, two hydrogen atoms will combine with one oxygen atom. The chemical formula for water is therefore:

 H_2O .



Worked Example 12: Formulae of covalent compounds

Question: Write the chemical formula for magnesium oxide

Answer

Step 1 : Write down the elements that make up the compound.

A molecule of magnesium oxide contains the elements magnesium and oxygen.

Step 2 : Determine the valency of each element

The valency of magnesium is 2, while the valency of oxygen is also 2. In a molecule of magnesium oxide, one atom of magnesium will combine with one atom of oxygen.

Step 3 : Write the chemical formula

The chemical formula for magnesium oxide is therefore:

MgO



Worked Example 13: Formulae of covalent compounds

Question: Write the chemical formula for copper (II) chloride.

Answer

Step 1 : Write down the elements that make up the compound.

A molecule of copper (II) chloride contains the elements copper and chlorine.

Step 2 : Determine the valency of each element

The valency of copper is 2, while the valency of chlorine is 1. In a molecule of copper (II) chloride, two atoms of chlorine will combine with one atom of copper.

Step 3 : Write the chemical formula

The chemical formula for copper (II) chloride is therefore:

 $CuCl_2$

4.9.2 The formulae of ionic compounds

The overall charge of an ionic compound will always be zero and so the negative and positive charge must be the same size. We can use this information to work out what the chemical formula of an ionic compound is if we know the charge on the individual ions. In the case of NaCl for example, the charge on the sodium is +1 and the charge on the chlorine is -1. The charges balance (+1-1=0) and therefore the ionic compound is neutral. In MgO, magnesium has a charge of +2 and oxygen has a charge of -2. Again, the charges balance and the compound is neutral. Positive ions are called **cations** and negative ions are called **anions**.

Some ions are made up of groups of atoms, and these are called **compound ions**. It is a good idea to learn the compound ions that are shown in table 4.2

Name of compound ion	formula
Carbonate	CO_{3}^{2-}
sulphate	SO_4^{2-}
Hydroxide	OH-
Ammonium	NH_4^+
Nitrate	NO_3^-
Hydrogen carbonate	HCO_3^-
Phosphate	PO_{4}^{3-}
Chlorate	CIO_3^-
Cyanide	CN^{-}
Chromate	$CrO_4{}^{2-}$
Permanganate	MnO_4^-

Table 4.2: Table showing common compound ions and their formulae

In the case of ionic compounds, the valency of an ion is the same as its charge (Note: valency is always expressed as a *positive* number e.g. valency of the chloride ion is 1 and not -1). Since an ionic compound is always *neutral*, the positive charges in the compound must balance out the negative. The following are some examples:



Worked Example 14: Formulae of ionic compounds

Question: Write the chemical formula for potassium iodide.

Answer

Step 1 : Write down the ions that make up the compound. Potassium iodide contains potassium and iodide ions.

Step 2 : Determine the valency and charge of each ion.

Potassium iodide contains the ions K^+ (valency = 1; charge = +1) and I^- (valency = 1; charge = -1). In order to balance the charge in a single molecule, one atom of potassium will be needed for every one atom of iodine.

Step 3 : Write the chemical formula

The chemical formula for potassium iodide is therefore:

ΚI



Worked Example 15: Formulae of ionic compounds

Question: Write the chemical formula for sodium sulphate.

Answer

Step 1 : Write down the ions that make up the compound.

Sodium sulphate contains sodium ions and sulphate ions.

Step 2 : Determine the valency and charge of each ion. Na⁺ (valency = 1; charge = +1) and SO₄²⁻ (valency = 2; charge = -2).

Step 3 : Write the chemical formula.

Two sodium ions will be needed to balance the charge of the sulphate ion. The chemical formula for sodium sulphate is therefore:

 $Na_2SO_4^{2-}$



Worked Example 16: Formulae of ionic compounds

Question: Write the chemical formula for calcium hydroxide.

Answer

Step 1 : Write down the ions that make up the compound. Calcium hydroxide contains calcium ions and hydroxide ions.

Step 2 : Determine the valency and charge of each ion.

Calcium hydroxide contains the ions Ca^{2+} (charge = +2) and OH^- (charge = -1). In order to balance the charge in a single molecule, two hydroxide ions will be needed for every ion of calcium.

Step 3 : Write the chemical formula.

The chemical formula for calcium hydroxide is therefore:

 $Ca(OH)_2$



Exercise: Chemical formulae

1. Copy and complete the table below:

Compound	Cation	Anion	Formula
	Na^+	CI-	
potassium bromide		Br [_]	
	NH_4^+	CI-	
potassium chromate			
			Pbl
potassium permanganate			
calcium phosphate			

- 2. Write the chemical formula for each of the following compounds:
 - (a) hydrogen cyanide
 - (b) carbon dioxide
 - (c) sodium carbonate
 - (d) ammonium hydroxide
 - (e) barium sulphate
 - (f) potassium permanganate

4.10 The Shape of Molecules

4.10.1 Valence Shell Electron Pair Repulsion (VSEPR) theory

The shape of a covalent molecule can be predicted using the Valence Shell Electron Pair Repulsion (VSEPR) theory. This is a model in chemistry that tries to predict the shapes of molecules. Very simply, VSEPR theory says that the electron pairs in a molecule will arrange themselves around the central atom of the molecule so that the repulsion between their negative charges is as small as possible. In other words, the electron pairs arrange themselves so that they are as far apart as they can be. Depending on the number of electron pairs in the molecule, it will have a different shape.

e la	
h	
N	

Definition: Valence Shell Electron Pair Repulsion Theory

Valence shell electron pair repulsion theory (VSEPR) is a model in chemistry, which is used to predict the shape of individual molecules, based upon the extent of their electron-pair repulsion.

VSEPR theory is based on the idea that the geometry of a molecule is mostly determined by repulsion among the pairs of electrons around a central atom. The pairs of electrons may be bonding or non-bonding (also called lone pairs). Only valence electrons of the central atom influence the molecular shape in a meaningful way.

4.10.2 Determining the shape of a molecule

To predict the shape of a covalent molecule, follow these steps:

Step 1:

Draw the molecule using Lewis notation. Make sure that you draw *all* the electrons around the molecule's central atom.

Step 2:

Count the number of electron pairs around the central atom.

Step 3:

Determine the basic geometry of the molecule using the table below. For example, a molecule with two electron pairs around the central atom has a *linear* shape, and one with four electron pairs around the central atom would have a *tetrahedral* shape. The situation is actually more

Geometry
linear
trigonal planar
tetrahedral
trigonal bipyramidal
octahedral

Table 4.3: The effect of electron pairs in determining the shape of molecules

complicated than this, but this will be discussed later in this section.

Figure 4.12 shows each of these shapes. Remember that the shapes are 3-dimensional, and so you need to try to imagine them in this way. In the diagrams, the shaded part represents those parts of the molecule that are 'in front', while the dashed lines represent those parts that are 'at the back' of the molecule.



Figure 4.12: Some common molecular shapes

Worked Example 17: The shapes of molecules

Question: Determine the shape of a molecule of O_2

Answer Step 1 : Draw the molecule using Lewis notation

Step 2 : Count the number of electron pairs around the central atom There are two electron pairs.

Step 3 : Determine the basic geometry of the molecule Since there are two electron pairs, the molecule must be linear. Worked Example 18: The shapes of molecules

Question: Determine the shape of a molecule of BF_3

Answer Step 1 : Draw the molecule using Lewis notation



Step 2 : Count the number of electron pairs around the central atom There are three electron pairs.

Step 3 : Determine the basic geometry of the molecule Since there are three electron pairs, the molecule must be trigonal planar.



Extension: More about molecular shapes

Determining the shape of a molecule can be a bit more complicated. In the examples we have used above, we looked only at the number of **bonding electron pairs** when we were trying to decide on the molecules' shape. But there are also other electron pairs in the molecules. These electrons, which are not involved in bonding but which are also around the central atom, are called **lone pairs**. The worked example below will give you an indea of how these lone pairs can affect the shape of the molecule.



Worked Example 19: Advanced

Question: Determine the shape of a molecule of NH_3

Answer Step 1 : Draw the molecule using Lewis notation





Step 2 : Count the number of electron pairs around the central atom There are four electron pairs.

Step 3 : Determine the basic geometry of the molecule

Since there are four electron pairs, the molecule must be tetrahedral.

Step 4 : Determine how many lone pairs are around the central atom

There is one lone pair of electrons and this will affect the shape of the molecule.

Step 5 : Determine the final shape of the molecule

The lone pair needs more space than the bonding pairs, and therefore pushes the three hydrogen atoms together a little more. The bond angles between the hydrogen and nitrogen atoms in the molecule become 106 degrees, rather than the usual 109 degrees of a tetrahedral molecule. The shape of the molecule is *trigonal pyramidal*.

Activity :: Group work : Building molecular models

In groups, you are going to build a number of molecules using marshmallows to represent the atoms in the molecule, and toothpicks to represent the bonds between the atoms. In other words, the toothpicks will hold the atoms (marshmallows) in the molecule together. Try to use different coloured marshmallows to represent different elements.

You will build models of the following molecules: HCl, CH_4 , H_2O , HBr and NH₃ For each molecule, you need to:

- Determine the basic geometry of the molecule
- Build your model so that the atoms are as far apart from each other as possible (remember that the electrons around the central atom will try to avoid the repulsions between them).
- Decide whether this shape is accurate for that molecule or whether there are any lone pairs that may influence it.
- Adjust the position of the atoms so that the bonding pairs are further away from the lone pairs.
- How has the shape of the molecule changed?
- Draw a simple diagram to show the shape of the molecule. It doesn't matter if it is not 100% accurate. This exercise is only to help you to visualise the 3-dimensional shapes of molecules.

Do the models help you to have a clearer picture of what the molecules look like? Try to build some more models for other molecules you can think of.

4.11 Oxidation numbers

When reactions occur, an exchange of electrons takes place. **Oxidation** is the *loss* of electrons from an atom, while **reduction** is the *gain* of electrons by an atom. By giving elements an oxidation number, it is possible to keep track of whether that element is losing or gaining electrons during a chemical reaction. The loss of electrons in one part of the reaction, must be balanced by a gain of electrons in another part of the reaction.



Definition: Oxidation number

A simplified way of understanding an oxidation number is to say that it is the charge an atom would have if it was in a compound composed of ions.

There are a number of rules that you need to know about oxidation numbers, and these are listed below. These will probably not make much sense at first, but once you have worked through some examples, you will soon start to understand!

- Rule 1: An element always has an oxidation number of zero, since it is neutral.
 In the reaction H₂ + Br₂ → 2HBr, the oxidation numbers of hydrogen and bromine on the left hand side of the equation are both zero.
- 2. **Rule 2:** In most cases, an atom that is part of a molecule will have an oxidation number that has the same numerical value as its valency.
- 3. Rule 3: Monatomic ions have an oxidation number that is equal to the charge on the ion. The chloride ion Cl^- has an oxidation number of -1, and the magnesium ion Mg^{2+} has an oxidation number of +2.
- 4. Rule 4: In a molecule, the oxidation number for the whole molecule will be zero, unless the molecule has a charge, in which case the oxidation number is equal to the charge.
- 5. **Rule 5:** Use a table of electronegativities to determine whether an atom has a positive or a negative oxidation number. For example, in a molecule of water, oxygen has a higher electronegativity so it must be negative because it attracts electrons more strongly. It will have a negative oxidation number (-2). Hydrogen will have a positive oxidation number (+1).
- 6. **Rule 6:** An oxygen atom usually has an oxidation number of -2, although there are some cases where its oxidation number is -1.
- 7. **Rule 7:** The oxidation number of hydrogen is usually +1. There are some exceptions where its oxidation number is -1.
- 8. Rule 8: In most compounds, the oxidation number of the halogens is -1.

Important: You will notice that the oxidation number of an atom is the same as its valency. Whether an oxidation number os positive or negative, is determined by the electronegativities of the atoms involved.

Worked Example 20: Oxidation numbers

Question: Give the oxidation numbers for all the atoms in the reaction between sodium and chlorine to form sodium chloride.

$$Na + Cl \rightarrow NaCl$$

Answer

Step 1 : Determine which atom will have a positive or negative oxidation number

Sodium will have a positive oxidation number and chlorine will have a negative oxidation number.

Step 2 : Determine the oxidation number for each atom

Sodium (group 1) will have an oxidation number of +1. Chlorine (group 7) will have an oxidation number of -1.

Step 3 : Check whether the oxidation numbers add up to the charge on the molecule

In the equation $Na + Cl \rightarrow NaCl$, the overall charge on the NaCl molecule is +1-1=0. This is correct since NaCl is neutral. This means that, in a molecule of NaCl, sodium has an oxidation number of +1 and chlorine has an oxidation number of -1.





Worked Example 21: Oxidation numbers

Question: Give the oxidation numbers for all the atoms in the reaction between hydrogen and oxygen to produce water. The unbalanced equation is shown below:

$$H_2 + O_2 \rightarrow H_2 O$$

Answer

Step 1 : Determine which atom will have a positive or negative oxidation number

Hydrogen will have a positive oxidation number and oxygen will have a negative oxidation number.

Step 2 : Determine the oxidation number for each atom

Hydrogen (group 1) will have an oxidation number of +1. Oxygen (group 6) will have an oxidation number of -2.

$\label{eq:step 3} \ensuremath{\mathsf{Step 3}}\xspace: \ensuremath{\mathsf{Check}}\xspace \ensuremath{\mathsf{whether}}\xspace \ensuremath{\mathsf{the}}\xspace \ensuremath{\mathsf{otherwide}}\xspace \ensuremath{\mathsf{step 3}}\xspace \ensuremath{\mathsf{check}}\xspace \ensuremath{\mathsf{otherwide}}\xspace \ensuremath{\mathsf{step 3}}\xspace \ensuremath{\mathsf{step 3}}\xspace \ensuremath{\mathsf{check}}\xspace \ensuremath{\mathsf{step 3}}\xspace \ensuremath{\mathsf{$

In the reaction $H_2 + O_2 \rightarrow H_2O$, the oxidation numbers for hydrogen and oxygen (on the left hand side of the equation) are zero since these are elements. In the water molecule, the sum of the oxidation numbers is 2(+1)-2=0. This is correct since the oxidation number of water is zero. Therefore, in water, hydrogen has an oxidation number of +1 and oxygen has an oxidation number of -2.



Worked Example 22: Oxidation numbers

Question: Give the oxidation number of sulfur in a sulphate (SO_4^{2-}) ion

Answer

Step 1 : Determine which atom will have a positive or negative oxidation number

Sulfur has a positive oxidation number and oxygen will have a negative oxidation number.

Step 2 : Determine the oxidation number for each atom

Oxygen (group 6) will have an oxidation number of -2. The oxidation number of sulfur at this stage is uncertain.

Step 3 : Determine the oxidation number of sulfur by using the fact that the oxidation numbers of the atoms must add up to the charge on the molecule In the polyatomic SO_4^{2-} ion, the sum of the oxidation numbers must be -2. Since there are four oxygen atoms in the ion, the total charge of the oxygen is -8. If the overall charge of the ion is -2, then the oxidation number of sulfur must be +6.

Exercise: Oxidation numbers

- 1. Give the oxidation numbers for each element in the following chemical compounds:
 - (a) NO_2
 - (b) BaCl₂
 - (c) H_2SO_4
- 2. Give the oxidation numbers for the reactants and products in each of the following reactions:
 - (a) $C + O_2 \rightarrow CO_2$
 - (b) $N_2 + 3H_2 \rightarrow 2NH_3$
 - (c) Magnesium metal burns in oxygen

4.12 Summary

- A **chemical bond** is the physical process that causes atoms and molecules to be attracted together and to be bound in new compounds.
- Atoms are more **reactive**, and therefore more likely to bond, when their outer electron orbitals are not full. Atoms are less reactive when these outer orbitals contain the maximum number of electrons. This explains why the noble gases do not combine to form molecules.
- There are a number of **forces** that act between atoms: attractive forces between the positive nucleus of one atom and the negative electrons of another; repulsive forces between like-charged electrons, and repulsion between like-charged nuclei.
- Chemical bonding occurs when the energy of the system is at its lowest.
- Bond length is the distance between the nuclei of the atoms when they bond.
- Bond energy is the energy that must be added to the system for the bonds to break.
- When atoms bond, electrons are either shared or exchanged.
- **Covalent bonding** occurs between the atoms of non-metals and involves a sharing of electrons so that the orbitals of the outermost energy levels in the atoms are filled.
- The valency of an atom is the number of bonds that it can form with other atoms.
- A **double** or **triple bond** occurs if there are two or three electron pairs that are shared between the same two atoms.
- A **dative covalent bond** is a bond between two atoms in which both the electrons that are shared in the bond come from the same atom.
- Lewis and Couper notation are two ways of representing molecular structure. In Lewis notation, dots and crosses are used to represent the valence electrons around the central atom. In Couper notation, lines are used to represent the bonds between atoms.
- Electronegativity measures how strongly an atom draws electrons to it.
- Electronegativity can be used to explain the difference between two types of covalent bonds: **polar covalent bonds** (between non-identical atoms) and **non-polar covalent bonds** (between identical atoms).
- An **ionic bond** occurs between atoms where the difference in electronegativity is greater than 2.1. An exchange of electrons takes place and the atoms are held together by the electrostatic force of attraction between oppositely-charged ions.
- Ionic solids are arranged in a crystal lattice structure.

- Ionic compounds have a number of specific properties, including their high melting and boiling points, brittle nature, the arrangement of solids in a lattice structure and the ability of ionic solutions to conduct electricity.
- A **metallic bond** is the electrostatic attraction between the positively charged nuclei of metal atoms and the delocalised electrons in the metal.
- Metals also have a number of properties, including their ability to conduct heat and electricity, their metallic lustre, the fact that they are both malleable and ductile, and their high melting point and density.
- The valency of atoms, and the way they bond, can be used to determine the **chemical formulae** of compounds.
- The shape of molecules can be predicted using the VSEPR theory, which uses the arrangement of electrons around the central atom to determine the most likely shape of the molecule.
- Oxidation numbers are used to determine whether an atom has gained or lost electrons during a chemical reaction.

Exercise: Summary exercise

- 1. Give one word/term for each of the following descriptions.
 - (a) The distance between two atoms in a molecule
 - (b) A type of chemical bond that involves the transfer of electrons from one atom to another.
 - (c) A measure of an atom's ability to attract electrons to it.
- 2. Which ONE of the following best describes the bond formed between an $\rm H^+$ ion and the $\rm NH_3$ molecule?
 - (a) Covalent bond
 - (b) Dative covalent (coordinate covalent) bond
 - (c) Ionic Bond
 - (d) Hydrogen Bond
- 3. Explain the meaning of each of the following terms:
 - (a) valency
 - (b) bond energy
 - (c) covalent bond
- 4. Which of the following reactions will not take place? Explain your answer.
 - (a) $H + H \rightarrow H_2$
 - (b) $Ne + Ne \rightarrow Ne_2$
 - (c) $I + I \rightarrow I_2$
- 5. Draw the Lewis structure for each of the following:
 - (a) calcium
 - (b) iodine
 - (c) hydrogen bromide (HBr)
 - (d) nitrogen dioxide (NO₂)
- 6. Given the following Lewis structure, where X and Y each represent a different element...



(a) What is the valency of X?

- (b) What is the valency of Y?
- (c) Which elements could X and Y represent?
- 7. A molecule of ethane has the formula C_2H_6 . Which of the following diagrams (Couper notation) accurately represents this molecule?

(a)
$$H H$$
 (b) H
 $| | |$
 $H - C = C - H$ $H - C - C - H$
 $| | |$
 $H H$ H H H H H

- 8. Potassium dichromate is dissolved in water.
 - (a) Give the name and chemical formula for each of the ions in solution.
 - (b) What is the chemical formula for potassium dichromate?
 - (c) Give the oxidation number for each element in potassium dichromate.

Chapter 5

Intermolecular Forces - Grade 11

In the previous chapter, we discussed the different forces that exist *between atoms* (intramolecular forces). When atoms are joined to one another they form molecules, and these molecules in turn have forces that bind them together. These forces are known as **intermolecular forces**, and we are going to look at them in more detail in this next section.



Definition: Intermolecular forces Intermolecular forces are forces that act between stable molecules.

You will also remember from the previous chapter, that we can describe molecules as being either **polar** or **non-polar**. A polar molecule is one in which there is a difference in electronegativity between the atoms in the molecule, such that the shared electron pair spends more time close to the atom that attracts it more strongly. The result is that one end of the molecule will have a slightly positive charge (δ^+), and the other end will have a slightly negative charge (δ^+). The molecule is said to be a **dipole**. However, it is important to remember that just because the bonds within a molecule are polar, the molecule itself may not necessarily be polar. The shape of the molecule may also affect its polarity. A few examples are shown in table 5.1 to refresh your memory!

5.1 Types of Intermolecular Forces

It is important to be able to recognise whether the molecules in a substance are polar or nonpolar because this will determine what type of inermolecular forces there are. This is important in explaining the properties of the substance.

1. Van der Waals forces

These intermolecular forces are named after a Dutch physicist called Johannes van der Waals (1837 -1923), who recognised that there were weak attractive and repulsive forces between the molecules of a gas, and that these forces caused gases to deviate from 'ideal gas' behaviour. Van der Waals forces are *weak* intermolecular forces, and can be divided into three types:

(a) Dipole-dipole forces

Figure 5.1 shows a simplified dipole molecule, with one end slightly positive and the other slightly negative.

When one dipole molecule comes into contact with another dipole molecule, the positive pole of the one molecule will be attracted to the negative pole of the other, and the molecules will be held together in this way (figure 5.2). Examples of molecules that are held together by dipole-dipole forces are HCl, FeS, KBr, SO₂ and NO₂.

(b) *lon-dipole forces*

As the name suggests, this type of intermolecular force exists between an ion and a dipole molecule. You will remember that an *ion* is a charged atom, and this will

Molecule	Chemical formula	Bond between atoms	Shape of molecule	Polarity of molecule
Hydrogen	H ₂	Covalent	Linear molecule H H	Non-polar
Hydrogen chlo- ride	HCI	Polar co- valent	Linear molecule ${f H}^{\delta^+}$ ——— ${f Cl}^{\delta^-}$	Polar
Carbon tetrafluo- romethane	CF ₄	Polar co- valent	Tetrahedral molecule $F^{\delta^{-}}$ $F^{\delta^{-}}$ $F^{\delta^{-}}$ $F^{\delta^{-}}$ $F^{\delta^{-}}$	Non-polar

Table 5.1: Polarity in molecules with different atomic bonds and molecular shapes



Figure 5.1: A simplified diagram of a dipole molecule



Figure 5.2: Two dipole molecules are held together by the attractive force between their oppositely charged poles

be attracted to one of the charged ends of the polar molecule. A positive ion will be attracted to the negative pole of the polar molecule, while a negative ion will be attracted to the positive pole of the polar molecule. This can be seen when sodium chloride (NaCl) dissolves in water. The positive sodium ion (Na⁺) will be attracted to the slightly negative oxygen atoms in the water molecule, while the negative chloride ion (Cl⁻) is attracted to the slightly positive hydrogen atom. These intermolecular forces weaken the ionic bonds between the sodium and chloride ions so that the sodium chloride dissolves in the water (figure 5.3).

(c) London forces

These intermolecular forces are also sometimes called 'dipole- induced dipole' or 'momentary dipole' forces. Not all molecules are polar, and yet we know that there are also intermolecular forces between non-polar molecules such as carbon dioxide. In



Figure 5.3: Ion-dipole forces in a sodium chloride solution

non-polar molecules the electronic charge is evenly distributed but it is possible that at a particular moment in time, the electrons might not be evenly distributed. The molecule will have a *temporary dipole*. In other words, each end of the molecules has a slight charge, either positive or negative. When this happens, molecules that are next to each other attract each other very weakly. These London forces are found in the halogens (e.g. F_2 and I_2), the noble gases (e.g. Ne and Ar) and in other non-polar molecules such as carbon dioxide and methane.

2. Hydrogen bonds

As the name implies, this type of intermolecular bond involves a hydrogen atom. The hydrogen must be attached to another atom that is strongly electronegative, such as oxygen, nitrogen or fluorine. Water molecules for example, are held together by hydrogen bonds between the hydrogen atom of one molecule and the oxygen atom of another (figure 5.4). Hydrogen bonds are stronger than van der Waals forces. It is important to note however, that both van der Waals forces and hydrogen bonds are weaker than the covalent and ionic bonds that exist between *atoms*.



Figure 5.4: Two representations showing the hydrogen bonds between water molecules: spacefilling model and structural formula.

5.2

Exercise: Types of intermolecular forces

1. Complete the following table by placing a tick to show which type of intermolecular force occurs in each substance:

Formula	Dipole- dipole	Momentary dipole	lon-dipole	hydrogen bond
HCI				
CO_2				
I_2				
H_2O				
KI(aq)				
NH_3				

2. In which of the substances above are the intermolecular forces...

(a) strongest

(b) weakest

5.2 Understanding intermolecular forces

The types of intermolecular forces that occur in a substance will affect its properties, such as its **phase**, **melting point** and **boiling point**. You should remember, if you think back to the kinetic theory of matter, that the *phase* of a substance is determined by how strong the forces are between its particles. The weaker the forces, the more likely the substance is to exist as a gas because the particles are far apart. If the forces are very strong, the particles are held closely together in a solid structure. Remember also that the *temperature* of a material affects the energy of its particles. The more energy the particles have, the more likely they are to be able to overcome the forces that are holding them together. This can cause a change in phase.



Definition: Boiling point

The temperature at which a material will change from being a liquid to being a gas.



Definition: Melting point

The temperature at which a material will change from being a solid to being a liquid.

Now look at the data in table 5.

Formula	Formula mass	Melting point (⁰ C)	Boiling point $({}^{0}C)$ at 1 atm
He	4	-270	-269
Ne	20	-249	-246
Ar	40	-189	-186
F_2	38	-220	-188
Cl_2	71	-101	-35
Br_2	160	-7	58
NH_3	17	-78	-33
H_2O	18	0	100
HF	20	-83	20

Table 5.2: Melting point and boiling point of a number of chemical substances

The melting point and boiling point of a substance, give us information about the *phase* of the substance at room temperature, and the *strength of the intermolecular forces*. The examples below will help to explain this.
Example 1: Fluorine (F₂)

Phase at room temperature

Fluorine (F₂) has a melting point of -220° C and a boiling point of -188° C. This means that for any temperature that is greater than -188° C, fluorine will be a gas. At temperatures below -220° C, fluorine would be a solid, and at any temperature inbetween these two, fluorine will be a liquid. So, at room temperature, fluorine exists as a gas.

Strength of intermolecular forces

What does this information tell us about the intermolecular forces in fluorine? In fluorine, these forces must be very weak for it to exist as a gas at room temperature. Only at temperatures below -188^oC will the molecules have a low enough energy that they will come close enough to each other for forces of attraction to act between the molecules. The intermolecular forces in fluorine are very weak **van der Waals** forces because the molecules are *non-polar*.

Example 2: Hydrogen fluoride (HF)

Phase at room temperature

For temperatures below -83° C, hydrogen fluoride is a solid. Between -83° C and 20° C, it exists as a liquid, and if the temperature is increased above 20° C, it will become a gas.

Strength of intermolecular forces

What does this tell us about the intermolecular forces in hydrogen fluoride? The forces are stronger than those in fluorine, because more energy is needed for fluorine to change into the gaseous phase. In other words, more energy is needed for the intermolecular forces to be overcome so that the molecules can move further apart. Intermolecular forces will exist between the hydrogen atom of one molecule and the fluorine atom of another. These are **hydrogen bonds**, which are stronger than van der Waals forces.

What do you notice about water? Luckily for us, water behaves quite differently from the rest of the halides. Imagine if water were like ammonia (NH_3) , which is a gas above a temperature of -33^{0} C! There would be no liquid water on the planet, and that would mean that no life would be able to survive here. The hydrogen bonds in water are particularly strong and this gives water unique qualities when compared to other molecules with hydrogen bonds. This will be discussed more in chapter **??** deals with this in more detail. You should also note that the strength of the intermolecular forces increases with an increase in formula mass. This can be seen by the increasing melting and boiling points of substances as formula mass increases.



Exercise: Applying your knowledge of intermolecular forces

Refer to the data in table 5.2 and then use your knowledge of different types of intermolecular forces to explain the following statements:

- The boiling point of F_2 is much lower than the boiling point of NH_3
- At room temperature, many elements exist naturally as gases
- The boiling point of HF is higher than the boiling point of CI_2
- The boiling point of water is much higher than HF, even though they both contain hydrogen bonds

5.3 Intermolecular forces in liquids

Intermolecular forces affect a number of properties in liquids:

• Surface tension

You may have noticed how some insects are able to walk across a water surface, and how leaves float in water. This is because of surface tension. In water, each molecule is held to the surrounding molecules by strong hydrogen bonds. Molecules in the centre of the liquid are completely surrounded by other molecules, so these forces are exerted in all directions. However, molecules at the surface do not have any water molecules above them to pull them upwards. Because they are only pulled sideways and downwards, the water molecules at the surface are held more closely together. This is called **surface tension**.



Figure 5.5: Surface tension in a liquid

• Capillarity

Activity :: Investigation : Capillarity

Half fill a beaker with water and hold a hollow glass tube in the centre as shown below. Mark the level of the water in the glass tube, and look carefully at the shape of the air-water interface in the tube. What do you notice?



At the air-water interface, you will notice a **meniscus**, where the water appears to dip in the centre. In the glass tube, the attractive forces between the glass and the water are stronger than the intermolecular forces between the water molecules. This causes the water to be held more closely to the glass, and a meniscus forms. The forces between the glass and the water also mean that the water can be 'pulled up' higher when it is in the tube than when it is in teh beaker. Capillarity is the surface tension that occurs in liquids that are inside tubes.

Evaporation

In a liquid, each particle has kinetic energy, but some particles will have more energy than others. We therefore refer to the *average* kinetic energy of the molecules when we describe the liquid. When the liquid is heated, those particles which have the highest energy will be able to overcome the intermolecular forces holding them in the liquid phase, and will become a gas. This is called **evaporation**. Evaporation occurs when a liquid changes to a gas. The stronger the intermolecular forces in a liquid, the higher the temperature of the molecules will have to be for it to become a gas. You should note that a liquid doesn't necessarily have to reach boiling point before evaporation can occur. Evaporation takes place all the time. You will see this if you leave a glass of water outside in the sun. Slowly the water level will drop over a period of time.

What happens then to the molecules of water that remain in the liquid? Remember that it was the molecules with the highest energy that left the liquid. This means that the average kinetic energy of the remaining molecules will decrease, and so will the *temperature* of the liquid.

A similar process takes place when a person sweats during exercise. When you exercise, your body temperature increases and you begin to release moisture (sweat) through the pores in your skin. The sweat quickly evaporates and causes the temperature of your skin to drop. This helps to keep your body temperature at a level that is suitable forit to function properly.



Transpiration in plants - Did you know that plants also 'sweat'? In plants, this is called *transpiration*, and a plant will lose water through spaces in the leaf surface called *stomata*. Although this water loss is important in the survival of a plant, if a plant loses too much water, it will die. Plants that live in very hot, dry places such as deserts, must be specially adapted to reduce the amount of water that transpires (evaporates) from their leaf surface. Desert plants have some amazing adaptations to deal with this problem! Some have hairs on their leaves, which reflect sunlight so that the temperature is not as high as it would be, while others have a thin waxy layer covering their leaves, which reduces water loss. Some plants are even able to close their stomata during the day when temperatures (and therefore transpiration) are highest.



Important: In the same way that intermolecular forces affect the properties of liquids, they also affect the properties of solids. For example, the stronger the intermolecular forces between the particles that make up the solid, the *harder* the solid is likely to be, and the higher its *melting point* is likely to be.

5.4 Summary

- Intermolecular forces are the forces that act between stable molecules.
- The type of intermolecular force in a substance, will depend on the nature of the molecules.
- **Polar molecules** have an unequal distribution of charge, meaning that one part of the molecule is slightly positive and the other part is slightly negative. **Non-polar molecules** have an equal distribution of charge.

97

- There are three types of **Van der Waal's forces**. These are dipole-dipole, ion-dipole and London forces (momentary dipole).
- Dipole-dipole forces exist between two polar molecules, for example between two molecules of hydrogen chloride.
- **Ion-dipole** forces exist between **ions and dipole molecules**. The ion is attracted to the part of the molecule that has an opposite charge to its own. An example of this is when an ionic solid such as sodium chloride dissolves in water.
- Momentary dipole forces occur between two non-polar molecules, where at some point there is an uequal distribution of charge in the molecule. For example, there are London forces between two molecules of carbon dioxide.
- Hydrogen bonds occur between hydrogen atoms and other atoms that have a high electronegativity such as oxygen, nitrogen and fluorine. The hydrogen atom in one molecule will be attracted to the nitrogen atom in another molecule, for example. There are hydrogen bonds between water molecules and between ammonia molecules.
- Intermolecular forces affect the properties of substances. For example, the stronger the intermolecular forces, the higher the melting point of that substance, and the more likely that substance is to exist as a solid or liquid. Its boiling point will also be higher.
- In liquids, properties such as surface tension, capillarity and evaporation are the result of intermolecular forces.

Exercise: Summary Exercise

- 1. Give one word or term for each of the following descriptions:
 - (a) The tendency of an atom in a molecule to attract bonding electrons.
 - (b) A molecule that has an unequal distribution of charge.
 - (c) A charged atom.
- For each of the following questions, choose the one correct answer from the list provided.
 - (a) The following table gives the melting points of various hydrides:

Hydride	Melting point (⁰ C)
HI	-50
NH_3	-78
H_2S	-83
CH_4	-184

In which of these hydrides does hydrogen bonding occur?

- i. HI only
- ii. NH₃ only
- iii. HI and NH_3 only
- iv. HI, NH_3 and H_2S

(IEB Paper 2, 2003)

(b) Refer to the list of substances below:

HCI, CI_2 , H_2O , NH_3 , N_2 , HF

Select the true statement from the list below:

- i. NH_3 is a non-polar molecule
- ii. The melting point of NH_3 will be higher than for CI_2
- iii. Ion-dipole forces exist between molecules of HF
- iv. At room temperature N_2 is usually a liquid

- The respective boiling points for four chemical substances are given below: Hydrogen sulphide -60°C Ammonia -33°C Hydrogen fluoride 20°C Water 100°C
 (a) Which are of the substances subjicts the strengest forces of strengtic
 - (a) Which one of the substances exhibits the strongest forces of attraction between its molecules in the liquid state?
 - (b) Give the name of the force responsible for the relatively high boiling points of ammonia and water and explain how this force originates.
 - (c) The shapes of the molecules of hydrogen sulphide and water are similar, yet their boiling points differ. Explain.

(IEB Paper 2, 2002)

Chapter 6

Solutions and solubility - Grade 11

We are surrounded by different types of solutions in our daily lives. Any solution is made up of a **solute** and a **solvent**. A **solute** is a substance that dissolves in a solvent. In the case of a salt (NaCl) solution, the salt crystals are the solute. A **solvent** is the substance in which the solute dissolves. In the case of the NaCl solution, the solvent would be the water. In most cases, there is always more of the solvent than there is of the solute in a solution.



Definition: Solutes and solvents

A **solute** is a substance that is dissolved in another substance. A solute can be a solid, liquid or gas. A **solvent** is the liquid that dissolves a solid, liquid, or gaseous solute.

6.1 Types of solutions

When a solute is mixed with a solvent, a *mixture* is formed, and this may be either *heterogeneous* or *homogeneous*. If you mix sand and water for example, the sand does not dissolve in the water. This is a **heterogeneous** mixture. When you mix salt and water, the resulting mixture is **homogeneous** because the solute has dissolved in the solvent.



Definition: Solution

In chemistry, a solution is a homogeneous mixture that consists of a solute that has been dissolved in a solvent.

A solution then is a homogeneous mixture of a solute and a solvent. Examples of solutions are:

- A solid solute dissolved in a liquid solvent e.g. sodium chloride dissolved in water.
- A gas solute dissolved in a liquid solvent e.g. carbon dioxide dissolved in water (fizzy drinks) or oxygen dissolved in water (aquatic ecosystems).
- A liquid solute dissolved in a liquid solvent e.g. ethanol in water.
- A solid solute in a solid solvent e.g. metal alloys.
- A gas solute in a gas solvent e.g. the homogeneous mixture of gases in the air that we breathe.

While there are many different types of solutions, most of those we will be discussing are liquids.

6.2 Forces and solutions

An important question to ask is why some solutes dissolve in certain solvents and not in others. The answer lies in understanding the interaction between the intramolecular and intermolecular forces between the solute and solvent particles.

Activity :: Experiment : Solubility

Aim: To investigate the solubility of solutes in different solvents. **Apparatus:**

Salt, vinegar, iodine, ethanol **Method**:

- 1. Mix half a teaspoon of salt in 100cm^3 of water
- 2. Mix half a teaspoon of vinegar (acetic acid) in 100cm³ of water
- 3. Mix a few grains of iodine in ethanol
- 4. Mix a few grains of iodine in 100 cm^3 of water

Results:

Record your observations in the table below:

Solute	Polar, non-polar or ionic solute	Solvent	Polar, non-polar or ionic solvent	Does solute dis- solve?
lodine		Ethanol		
lodine		Water		
Vinegar		Water		
Salt		Water		

You should have noticed that in some cases, the solute dissolves in the solvent, while in other cases it does not.

Conclusions:

In general, polar and ionic solutes dissolve well in polar solvents, while non-polar solutes dissolve well in non-polar solvents. An easy way to remember this is that 'like dissolves like', in other words, if the solute and the solvent have similar intermolecular forces, there is a high possibility that dissolution will occur. This will be explained in more detail below.

• Non-polar solutes and non-polar solvents (e.g. iodine and ether)

lodine molecules are non-polar, and the forces between the molecules are weak van der Waals forces. There are also weak van der Waals forces between ether molecules. Because the intermolecular forces in both the solute and the solvent are similar, it is easy for these to be broken in the solute, allowing the solute to move into the spaces between the molecules of the solvent. The solute dissolves in the solvent.

• Polar solutes and polar solvents (e.g. salt and water)

There are strong electrostatic forces between the ions of a salt such as sodium chloride. There are also strong hydrogen bonds between water molecules. Because the strength of the intermolecular forces in the solute and solvent are similar, the solute will dissolve in the solvent.

6.3 Solubility

You may have noticed sometimes that, if you try to dissolve salt (or some other solute) in a small amount of water, it will initially dissolve, but then appears not to be able to dissolve any further when you keep adding more solute to the solvent. This is called the **solubility** of the solution. Solubility refers to the maximum amount of solute that will dissolve in a solvent under certain conditions.



Definition: Solubility

Solubility is the ability of a given substance, the solute, to dissolve in a solvent. If a substance has a high solubility, it means that lots of the solute is able to dissolve in the solvent.

So what factors affect solubility? Below are some of the factors that affect solubility:

- the quantity of solute and solvent in the solution
- the temperature of the solution
- other compounds in the solvent affect solubility because they take up some of the spaces between molecules of the solvent, that could otherwise be taken by the solute itself
- the strength of the forces between particles of the solute, and the strength of forces between particles of the solvent

Activity :: Experiment : Factors affecting solubility Aim:

To determine the effect of temperature on solubility **Method:**

- 1. Measure 100cm^3 of water into a beaker
- 2. Measure 100 g of salt and place into another beaker
- 3. Slowly pour the salt into the beaker with the water, stirring it as you add. Keep adding salt until you notice that the salt is not dissolving anymore.
- 4. Record the amount of salt that has been added to the water and the temperature of the solution.
- 5. Now increase the temperature of the water by heating it over a bunsen burner.
- 6. Repeat the steps above so that you obtain the solubility limit of salt at this higher temperature. You will need to start again with new salt and water!
- 7. Continue to increase the temperature as many times as possible and record your results.

Results:

Record your results in the table below:

Temp (⁰ C)	Amount of solute that dissolves in 100 cm 3 of water (g)

As you increase the temperature of the water, are you able to dissolve *more* or *less* salt?

Conclusions:

6.3

As the temperature of the solution increases, so does the amount of salt that will dissolve. The solubility of sodium chloride increases as the temperature increases.

Exercise: Investigating the solubility of salts

The data table below gives the solubility (measured in grams of salt per 100 g water) of a number of different salts at various temperatures. Look at the data and then answer the questions that follow.

	Solubility (g salt per 100 g H_2O)		
Temp (⁰ C)	KNO ₃	K_2SO_4	NaCl
0	13.9	7.4	35.7
10	21.2	9.3	35.8
20	31.6	11.1	36.0
30	45.3	13.0	36.2
40	61.4	14.8	36.5
50	83.5	16.5	36.8
60	106.0	18.2	37.3

- 1. On the same set of axes, draw line graphs to show how the solubility of the three salts changes with an increase in temperature.
- 2. Describe what happens to salt solubility as temperature increases. Suggest a reason why this happens.
- 3. Write an equation to show how each of the following salts ionises in water:
 - (a) KNO_3
 - (b) K_2SO_4
- 4. You are given three beakers, each containing the same amount of water. 5 g KNO_3 is added to beaker 1, 5 g K_2SO_4 is added to beaker 2 and 5 g NaCl is added to beaker 3. The beakers are heated over a bunsen burner until the temperature of their solutions is $60^{\circ}C$.
 - (a) Which salt solution will have the highest conductivity under these conditions?
 - (b) Explain your answer.

Exercise: Experiments and solubility

Two grade 10 learners, Siphiwe and Ann, wish to separately investigate the solubility of potassium chloride at room temperature. They follow the list of instructions shown below, using the apparatus that has been given to them:

Method:

- 1. Determine the mass of an empty, dry evaporating basin using an electronic balance and record the mass.
- 2. Pour 50 ml water into a 250 ml beaker.

- 3. Add potassium chloride crystals to the water in the beaker in small portions.
- 4. Stir the solution until the salt dissolves.
- 5. Repeat the addition of potassium chloride (steps a and b) until no more salt dissolves and some salt remains undissolved.
- 6. Record the temperature of the potassium chloride solution.
- 7. Filter the solution into the evaporating basin.
- Determine the mass of the evaporating basin containing the solution that has passed through the filter (the filtrate) on the electronic balance and record the mass.
- 9. Ignite the Bunsen burner.
- 10. Carefully heat the filtrate in the evaporating basin until the salt is dry.
- 11. Place the evaporating basin in the desiccator (a large glass container in which there is a dehydrating agent like calcium sulphate that absorbs water) until it reaches room temperature.
- 12. Determine the mass of the evaporating basin containing the dry cool salt on the electronic balance and record the mass.

	Siphiwe's	Ann's
	results	results
Temperature (⁰ C)	15	26
Mass of evaporating basin (g)	65.32	67.55
Mass of evaporating basin $+$ salt solution (g)	125.32	137.55
Mass of evaporating basin $+$ salt (g)	81.32	85.75

- 1. Calculate the solubility of potassium chloride, using the data recorded by
 - (a) Siphiwe
 - (b) Ann

A reference book lists the solubility of potassium chloride as 35.0 g per 100 ml of water at 25^{0} C.

- (c) Give a reason why you think each obtained results different from each other and the value in the reference book.
- Siphiwe and Ann now expand their investigation and work together. They
 investigate the solubility of potassium chloride at different temperatures but
 also the solubility of copper (II) sulphate at these same temperatures. They
 collect and write up their results as follows:

In each experiment we used 50 ml of water in the beaker. We found the following masses of substance dissolved in the 50 ml of water. At 0^{0} C, mass of potassium chloride is 14.0 g and copper sulphate is 14.3 g. At 10^{0} C, 15.6 g and 17.4 g respectively. At 20^{0} C, 17.3 g and 20.7 g respectively. At 40^{0} C, potassium chloride mass is 20.2 g and copper sulphate is 28.5 g, at 60^{0} C, 23.1 g and 40.0 g and lastly at 80^{0} C, the masses were 26.4 g and 55.0 g respectively.

- (a) From the record of data provided above, draw up a neat table to record Siphiwe and Ann's results.
- (b) Identify the dependent and independent variables in their investigation.
- (c) Choose an appropriate scale and plot a graph of these results.
- (d) From the graph, determine:
 - i. the temperature at which the solubility of copper sulphate is 50 g per 50 ml of water.
 - ii. the maximum number of grams of potassium chloride which will dissolve in 100 ml of water at 70^{0} C.

(IEB Exemplar Paper 2, 2006)

6.4 Summary

- In chemistry, a solution is a homogenous mixture of a solute in a solvent.
- A solute is a substance that dissolves in a solute. A solute can be a solid, liquid or gas.
- A solvent is a substance in which a solute dissolves. A solvent can also be a solid, liquid or gas.
- Examples of solutions include salt solutions, metal alloys, the air we breathe and gases such as oxygen and carbon dioxide dissolved in water.
- Not all solutes will dissolve in all solvents. A general rule is the **like dissolves like**. Solutes and solvents that have similar intermolecular forces are more likely to dissolve.
- Polar and ionic solutes will be more likely to dissolve in polar solvents, while non-polar solutes will be more likely to dissolve in polar solvents.
- **Solubility** is the extent to which a solute is able to dissolve in a solvent under certain conditions.
- Factors that affect solubility are the **quantity of solute and solvent**, **temperature**, the **intermolecular forces** in the solute and solvent and **other substances** that may be in the solvent.

Exercise: Summary Exercise

- 1. Give one word or term for each of the following descriptions:
- (a) A type of mixture where the solute has completely dissolved in the solvent.
 - (b) A measure of how much solute is dissolved in a solution.
 - (c) Forces between the molecules in a substance.
- For each of the following questions, choose the one correct answer from the list provided.
 - A Which one of the following will readily dissolve in water?
 - i. I₂(s)
 - ii. Nal(s)
 - iii. $CCI_4(I)$
 - iv. $BaSO_4(s)$
 - (IEB Paper 2, 2005)
 - b In which of the following pairs of substances will the dissolving process happen most readily?

	Solute	Solvent
А	S_8	H_2O
В	KCI	CCI_4
С	KNO_3	H_2O
D	NH_4CI	CCI_4
(IEB Paper 2, 2004)		

3. Which one of the following three substances is the most soluble in pure water at room temperature?

Hydrogen sulphide, ammonia and hydrogen fluoride

 Briefly explain in terms of intermolecular forces why solid iodine does not dissolve in pure water, yet it dissolves in xylene, an organic liquid at room temperature.

(IEB Paper 2, 2002)

Chapter 7

Atomic Nuclei - Grade 11

Nuclear physics is the branch of physics which deals with the **nucleus** of the atom. Within this field, some scientists focus their attention on looking at the *particles* inside the nucleus and understanding how they interact, while others classify and interpret the *properties* of nuclei. This detailed knowledge of the nucleus makes it possible for *technological advances* to be made. In this next chapter, we are going to touch on each of these different areas within the field of nuclear physics.

7.1 Nuclear structure and stability

You will remember from an earlier chapter that an atom is made up of different types of particles: protons (positive charge) neutrons (neutral) and electrons (negative charge). The nucleus is the part of the atom that contains the protons and the neutrons, while the electrons are found in energy orbitals around the nucleus. The protons and neutrons together are called **nucleons**. It is the nucleus that makes up most of an atom's *atomic mass*, because an electron has a very small mass when compared with a proton or a neutron.

Within the nucleus, there are different forces which act between the particles. The **strong nuclear force** is the force between two or more nucleons, and this force binds protons and neutrons together inside the nucleus. This force is most powerful when the nucleus is small, and the nucleons are close together. The **electromagnetic force** causes the repulsion between like-charged (positive) protons. In a way then, these forces are trying to produce opposite effects in the nucleus. The strong nuclear force acts to hold all the protons and neutrons close together, while the electromagnetic force acts to push protons further apart. In atoms where the nuclei are small, the strong nuclear force overpowers the electromagnetic force. However, as the nucleus gets bigger (in elements with a higher number of nucleons), the electromagnetic force becomes greater than the strong nuclear force. In these nuclei, it becomes possible for particles and energy to be ejected from the nucleus. These nuclei are called **unstable**. The particles and energy that a nucleus releases are referred to as **radiation**, and the atom is said to be **radioactive**. We are going to look at these concepts in more detail in the next few sections.

7.2 The Discovery of Radiation

Radioactivity was first discovered in 1896 by a French scientist called Henri Becquerel while he was working on phosphorescent materials. He happened to place some uranium crystals on black paper that he had used to cover a piece of film. When he looked more carefully, he noticed that the film had lots of patches on it, and that this did not happen when other elements were placed on the paper. He eventually concluded that some rays must be coming out of the uranium crystals to produce this effect.

His observations were taken further by the Polish scientist Marie Curie and her husband Pierre, who increased our knowledge of radioactive elements. In 1903, Henri, Marie and Pierre were

awarded the Nobel Prize in Physics for their work on radioactive elements. This award made Marie the first woman ever to receive a Nobel Prize. Marie Curie and her husband went on to discover two new elements, which they named **polonium** (Po) after Marie's home country, and **radium** (Ra) after its highly radioactive characteristics. For these dicoveries, Marie was awarded a Nobel Prize in Chemistry in 1911, making her one of very few people to receive two Nobel Prizes.



7.3

Marie Curie died in 1934 from aplastic anemia, which was almost certainly partly due to her massive exposure to radiation during her lifetime. Most of her work was carried out in a shed without safety measures, and she was known to carry test tubes full of radioactive isotopes in her pockets and to store them in her desk drawers. By the end of her life, not only was she very ill, but her hands had become badly deformed due to their constant exposure to radiation. Unfortunately it was only later in her life that the full dangers of radiation were realised.

7.3 Radioactivity and Types of Radiation

In section 7.1, we discussed that when a nucleus is unstable it can emit particles and energy. This is called **radioactive decay**.



Definition: Radioactive decay

Radioactive decay is the process in which an unstable atomic nucleus loses energy by emitting particles or electromagnetic waves. **Radiation** is the name for the emitted particles or electromagnetic waves.

When a nucleus undergoes radioactive decay, it emits radiation and the nucleus is called radioactive. We are exposed to small amounts of radiation all the time. Even the rocks around us emit radiation! However some elements are far more radioactive than others. *Isotopes* tend to be less stable because they contain a larger number of nucleons than 'non-isotopes' of the same element. These radioactive isotopes are called **radioisotopes**.

Radiation can be emitted in different forms. There are three main types of radiation: alpha, beta and gamma radiation. These are shown in figure 7.1, and are described below.



Figure 7.1: Types of radiation

7.3.1 Alpha (α) particles and alpha decay

An alpha particle is made up of two protons and two neutrons bound together. This type of radiation has a *positive charge*. An alpha particle is sometimes represented using the chemical symbol He^{2+} , because it has the same structure as a Helium atom (two neutrons and two protons) which is missing its two electrons, hence the overall charge of +2. Alpha particles have very low penetration power. Penetration power describes how easily the particles can pass through another material. Because alpha particles have a *low* penetration power, it means that even something as thin as a piece of paper or the outside layer of the human skin, will absorb these particles so that they can't go any further.

Alpha decay occurs because the nucleus has too many protons, and this causes a lot of repulsion between these like charges. To try to reduce this repulsion, the nucleus emits an α particle. This can be seen in the decay of Americium (Am) to Neptunium (Np).

Example:

$$^{241}_{95}$$
Am $\rightarrow ^{237}_{93}$ Np + α particle

Let's take a closer look at what has happened during this reaction. Americium (Z = 95; A = 241) undergoes α decay and releases one alpha particle (i.e. 2 protons and 2 neutrons). The atom now has only 93 protons (Z = 93). On the periodic table, the element which has 93 protons (Z = 93) is called Neptunium. Therefore, the Americium atom has become a Neptunium atom. The atomic mass of the neptunium atom is 237 (A = 237) because 4 nucleons (2 protons and 2 neutrons) were emitted from the atom of Americium.

7.3.2 Beta (β) particles and beta decay

In certain types of radioactive nuclei that have too many neutrons, a neutron may be converted into a proton, an electron and another particle (called a *neutrino*). The high energy electrons that are released in this way are called **beta particles**. Beta particles have a higher penetration power than alpha particles and are able to pass through thicker materials such as paper.

The diagram below shows what happens during β decay:



Figure 7.2: β decay in a hydrogen atom

During beta decay, the number of neutrons in the atom decreases by one, and the number of protons increases by one. Since the number of protons before and after the decay is different,

the atom has changed into a different element. In figure 7.2, Hydrogen has become Helium. The beta decay of the Hydrogen-3 atom can be represented as follows:

 $^{3}_{1}\text{H} \rightarrow ^{3}_{2}\text{He} + \beta \text{particle} + \bar{\nu}$



When scientists added up all the energy from the neutrons, protons and electrons involved in β -decays, they noticed that there was always some energy missing. We know that energy is always conserved, which led Wolfgang Pauli in 1930 to come up with the idea that another particle, which was not detected yet, also had to be involved in the decay. He called this particle the neutrino (Italian for "little neutral one"), because he knew it had to be neutral, have little or no mass, and interact only very weakly, making it very hard to find experimentally! The neutrino was finally identified experimentally about 25 years after Pauli first thought of it.

Due to the radioactive processes inside the sun, each 1 cm^2 patch of the earth receives 70 billion (70×10^9) neutrinos each second! Luckily neutrinos only interact very weakly so they do not harm our bodies when billions of them pass through us every second.

7.3.3 Gamma (γ) rays and gamma decay

When particles inside the nucleus collide during radioactive decay, energy is released. This energy can leave the nucleus in the form of waves of electromagnetic energy called gamma rays. Gamma radiation is part of the electromagnetic spectrum, just like visible light. However, unlike visible light, humans cannot see gamma rays because they are at a higher frequency and a higher energy. Gamma radiation has no mass or charge. This type of radiation is able to penetrate most common substances, including metals. The only substances that can absorb this radiation are thick lead and concrete.

Gamma decay occurs if the nucleus is at too high an energy level. Since gamma rays are part of the electromagnetic spectrum, they can be thought of as waves or particles. Therefore in gamma decay, we can think of a ray or a particle (called a photon) being released. The atomic number and atomic mass remain unchanged.

Table 7.1 summarises and compares the three types of radioactive decay that have been discussed.

Type of decay	Particle/ray released	Change in element	Penetration power
Alpha (α)	lpha particle (2 protons and 2 neutrons)	Yes	Low
Beta (β)	β particle (electron)	Yes	Medium
Gamma (γ)	γ ray (electromagnetic energy)	No	High



Worked Example 23: Radioactive decay

Question: The isotope ${}^{241}_{95}$ Pb undergoes radioactive decay and loses two alpha particles.



Figure 7.3: γ decay in a helium atom

- 1. Write the chemical formula of the element that is produced as a result of the decay.
- 2. Write an equation for this decay process.

Answer

Step 1 : Work out the number of protons and/or neutrons that the radioisotope loses during radioactive decay

One α particle consists of two protons and two neutrons. Since two α particles are released, the total number of protons lost is four and the total number of neutrons lost is also four.

Step 2 : Calculate the atomic number (Z) and atomic mass number (A) of the element that is formed.

$$Z = 95 - 4 = 91$$

 $A = 241 - 4 = 237$

Step 3 : Refer to the periodic table to see which element has the atomic number that you have calculated.

The element that has Z = 91 is Protactinium (Pa).

Step 4 : Write the symbol for the element that has formed as a result of radioactive decay.

 $^{237}_{91}$ Pa

Step 5 : Write an equation for the decay process.

 $^{241}_{95}Pb \rightarrow ^{237}_{91}Pa + 2$ protons + 2 neutrons

Activity :: Discussion : Radiation

In groups of 3-4, discuss the following questions:

• Which of the three types of radiation is most dangerous to living creatures (including humans!)

- What can happen to people if they are exposed to high levels of radiation?
- What can be done to protect yourself from radiation (Hint: Think of what the radiologist does when you go for an X-ray)?

?

Exercise: Radiation and radioactive elements

- 1. There are two main forces inside an atomic nucleus:
 - (a) Name these two forces.
 - (b) Explain why atoms that contain a greater number of nucleons are more likely to be radioactive.
- 2. The isotope $\frac{241}{95}$ Pb undergoes radioactive decay and loses three alpha particles.
 - (a) Write the chemical formula of the element that is produced as a result of the decay.
 - (b) How many nucleons does this element contain?
- 3. Complete the following equation:

 $^{210}_{82}Am \rightarrow (alpha decay)$

- 4. Radium-228 decays by emitting a beta particle. Write an equation for this decay process.
- 5. Describe how gamma decay differs from alpha and beta decay.

7.4 Sources of radiation

The sources of radiation can be either natural or man-made.

7.4.1 Natural background radiation

Cosmic radiation

The Earth, and all living things on it, are constantly bombarded by radiation from space. Charged particles from the sun and stars interact with the Earth's atmosphere and magnetic field to produce a shower of radiation, mostly beta and gamma radiation. The amount of cosmic radiation varies in different parts of the world because of differences in elevation and also the effects of the Earth's magnetic field.

• Terrestrial Radiation

Radioactive material is found throughout nature. It occurs naturally in the soil, water, and vegetation. The major isotopes that are of concern are uranium and the decay products of uranium, such as thorium, radium, and radon. Low levels of uranium, thorium, and their decay products are found everywhere. Some of these materials are ingested (taken in) with food and water, while others are breathed in. The dose of radiation from terrestrial sources varies in different parts of the world.



Cosmic and terrestrial radiation are not the only natural sources. All people have radioactive potassium-40, carbon-14, lead-210 and other isotopes inside their bodies from birth.

7.4.2 Man-made sources of radiation

Although all living things are exposed to natural background radiation, there are other sources of radiation. Some of these will affect most members of the public, while others will only affect those people who are exposed to radiation through their work.

• Members of the Public

Man-made radiation sources that affect members of the public include televisions, tobacco (polonium-210), combustible fuels, smoke detectors (americium), luminous watches (tritium) and building materials. By far, the most significant source of man-made radiation exposure to the public is from medical procedures, such as diagnostic x-rays, nuclear medicine, and radiation therapy. Some of the major isotopes involved are I-131, Tc-99m, Co-60, Ir-192, and Cs-137. The production of nuclear fuel using uranium is also a source of radiation for the public, as is fallout from nuclear weapons testing or use.

• Individuals who are exposed through their work

Any people who work in the following environments are exposed to radiation at some time: radiology (X-ray) departments, nuclear power plants, nuclear medicine departments and radiation oncology (the study of cancer) departments. Some of the isotopes that are of concern are cobalt-60, cesium-137, americium-241, and others.



Radiation therapy (or radiotherapy) uses ionising radiation as part of cancer treatment to control malignant cells. In cancer, a malignant cell is one that divides very rapidly to produce many more cells. These groups of dividing cells can form a growth or **tumour**. The malignant cells in the tumour can take nutrition away from other healthy body cells, causing them to die, or can increase the pressure in parts of the body because of the space that they take up. Radiation therapy uses radiation to try to target these malignant cells and kill them. However, the radiation can also damage other, healthy cells in the body. To stop this from happening, shaped radiation beams are aimed from several angles to intersect at the tumour, so that the radiation dose here is much higher than in the surrounding, healthy tissue. But even doing this doesn't protect all the healthy cells, and that is why people have side-effects to this treatment.

Note that radiation therapy is different from chemotherapy, which uses *chemicals*, rather than radiation, to destroy malignant cells. Generally, the side effects of chemotherapy are greater because the treatment is not as localised as it is with radiation therapy. The chemicals travel throughout the body, affecting many healthy cells.

7.5 The 'half-life' of an element



Definition: Half-life

The half-life of an element is the time it takes for half the atoms of a radioisotope to decay into other atoms.

Radioisotope	Chemical symbol	Halt-life
Polonium-212	Po-212	0.16 seconds
Sodium-24	Na-24	15 hours
Strontium-90	Sr-90	28 days
Cobalt-60	Co-60	5.3 years
Caesium-137	Cs-137	30 years
Carbon-14	C-14	5 760 years
Calcium	Ca	100 000 years
Beryllium	Be	2 700 000 years
Uranium-235	U-235	7.1 billion years

Table 7.2: Table showing the half-life of a number of elements

So, in the case of Sr-90, it will take 28 days for half of the atoms to decay into other atoms. It will take another 28 days for half of the remaining atoms to decay. Let's assume that we have a sample of strontium that weighs 8g. After the first 28 days there will be:

$$1/2 \times 8 = 4$$
 g Sr-90 left

After 56 days, there will be:

$$1/2 \ge 4 \text{ g} = 2 \text{ g Sr-90 left}$$

After 84 days, there will be:

$$1/2 \ge 2 = 1 = 1 = 1$$

If we convert these amounts to a *fraction* of the original sample, then after 28 days 1/2 of the sample remains undecayed. After 56 days 1/4 is undecayed and after 84 days, 1/8 and so on.

Activity :: Group work : Understanding half-life Work in groups of 4-5 You will need: 16 sheets of A4 paper per group, scissors, 2 boxes per group, a marking pen and timer/stopwatch.

What to do:

- Your group should have two boxes. Label one 'decayed' and the other 'radioactive'.
- Take the A4 pages and cut each into 4 pieces of the same size. You should now have 64 pieces of paper. Stack these neatly and place them in the 'radioactive' box. The paper is going to represent some radioactive material.
- Set the timer for one minute. After one minute, remove half the sheets of paper from the radioactive box and put them in the 'decayed' box.
- Set the timer for another minute and repeat the previous step, again removing half the pieces of paper that are left in the radioactive box and putting them in the decayed box.
- Repeat this process until 8 minutes have passed. You may need to start cutting your pieces of paper into even smaller pieces as you progress.

Questions:

- 1. How many pages were left in the radioactive box after...
 - (a) 1 minute
 - (b) 3 minutes

7.5

- (c) 5 minutes
- 2. What percentage (%) of the pages were left in the radioactive box after...
 - (a) 2 minutes
 - (b) 4 minutes
- 3. After how many minutes is there 1/128 of radioactive material remaining?
- 4. What is the half-life of the 'radioactive' material in this exercise?



Worked Example 24: Half-life 1

Question: A 100 g sample of Cs-137 is allowed to decay. Calculate the mass of Cs-137 that will be left after 90 years

Answer

Step 1 : You need to know the half-life of Cs-137 The half-life of Cs-137 is 30 years.

Step 2 : Determine how many times the quantity of sample will be halved in 90 years.

If the half-life of Cs-137 is 30 years, and the sample is left to decay for 90 years, then the number of times the quantity of sample will be halved is 90/30 = 3.

Step 3 : Calculate the quantity that will be left by halving the mass of Cs-137 three times

1. After 30 years, the mass left is 100 g \times 1/2 = 50 g

2. After 60 years, the mass left is 50 g \times 1/2 = 25 g

3. After 90 years, the mass left is 25 g \times 1/2 = 12.5 g

Note that a quicker way to do this calculation is as follows: Mass left after 90 years = $(1/2)^3 \times 100 \text{ g} = 12.5 \text{ g}$ (The exponent is the number of times the quantity is halved)



Worked Example 25: Half-life 2

Question: An 80 g sample of Po-212 decays until only 10 g is left. How long did it take for this decay to take place?

Answer

Step 1 : Calculate the fraction of the original sample that is left after decay Fraction remaining =10~g/80~g=1/8

Step 2 : Calculate how many half-life periods of decay (x) must have taken place for 1/8 of the original sample to be left

$$(\frac{1}{2})^x = \frac{1}{8}$$

Therefore, x = 3

7.6

Step 3 : Use the half-life of Po-212 to calculate how long the sample was left to decay

The half-life of Po-212 is 0.16 seconds. Therefore if there were three periods of decay, then the total time is 0.16 \times 3. The time that the sample was left to decay is 0.48 seconds.

Exercise: Looking at half life

- 1. Imagine that you have 100 g of Na-24.
 - (a) What is the half life of Na-24?
 - (b) How much of this isotope will be left after 45 hours?
 - (c) What percentage of the original sample will be left after 60 hours?
- 2. A sample of Sr-90 is allowed to decay. After 84 days, 10 g of the sample remains.
 - (a) What is the half life of Sr-90?
 - (b) How much Sr-90 was in the original sample?
 - (c) How much Sr-90 will be left after 112 days?

7.6 The Dangers of Radiation

Natural radiation comes from a variety of sources such as the rocks, sun and from space. However, when we are exposed to large amounts of radiation, this can cause damage to cells. γ radiation is particularly dangerous because it is able to penetrate the body, unlike α and β particles whose penetration power is less. Some of the dangers of radiation are listed below:

• Damage to cells

Radiation is able to penetrate the body, and also to penetrate the membranes of the cells within our bodies, causing massive damage. *Radiation poisoning* occurs when a person is exposed to large amounts of this type of radiation. Radiation poisoning damages tissues within the body, causing symptoms such as diarrhoea, vomiting, loss of hair and convulsions.

• Genetic abnormalities

When radiation penetrates cell membranes, it can damage chromosomes within the nucleus of the cell. The chromosomes contain all the genetic information for that person. If the chromosomes are changed, this may lead to genetic abnormalities in any children that are born to the person who has been exposed to radiation. Long after the nuclear disaster of Chernobyl in Russia in 1986, babies were born with defects such as missing limbs and abnormal growths.

• Cancer

Small amounts of radiation can cause cancers such as leukemia (cancer of the blood)

7.7 The Uses of Radiation

However, despite the many dangers of radiation, it does have many powerful uses, some of which are listed below:

• Medical Field

Radioactive *chemical tracers* emitting γ rays can give information about a person's internal anatomy and the functioning of specific organs. The radioactive material may be injected into the patient, from where it will target specific areas such as bones or tumours. As the material decays and releases radiation, this can be seen using a special type of camera or other instrument. The radioactive material that is used for this purpose must have a short half-life so that the radiation can be detected quickly and also so that the material is quickly removed from the patient's body. Using radioactive materials for this purpose can mean that a tumour or cancer may be diagnosed long before these would have been detected using other methods such as X-rays.

Radiation may also be used to sterilise medical equipment.

Activity :: Research Project : The medical uses of radioisotopes

Carry out your own research to find out more about the radioisotopes that are used to diagnose diseases in the following parts of the body:

- thyroid gland
- kidneys
- brain

In each case, try to find out...

- 1. which radioisotope is used
- 2. what the sources of this radioisotope are
- 3. how the radioisotope enters the patient's body and how it is monitored

• Biochemistry and Genetics

Radioisotopes may be used as tracers to label molecules so that chemical processes such as DNA replication or amino acid transport can be traced.

• Food preservation

Irradiation of food can stop vegetables or plants from sprouting after they have been harvested. It also kills bacteria and parasites, and controls the ripening of fruits.

Environment

Radioisotopes can be used to trace and analyse pollutants.

• Archaeology and Carbon dating

Natural radioisotopes such as C-14 can be used to determine the age of organic remains. All living organisms (e.g. trees, humans) contain carbon. Carbon is taken in by plants and trees through the process of photosynthesis in the form of carbon dioxide and is then converted into organic molecules. When animals feed on plants, they also obtain carbon through these organic compounds. Some of the carbon in carbon dioxide is the radioactive C-14, while the rest is a non-radioactive form of carbon. When an organism dies, no more carbon is taken in and there is a limited amount of C-14 in the body. From this point onwards, C-14 begins its radioactive decay. When scientists uncover remains, they are able to estimate the age of the remains by seeing how much C-14 is left in the body relative to the amount of non-radioactive carbon. The less C-14 there is, the older the remains because radioactive decay must have been taking place for a long time. Because scientists know the exact rate of decay of C-14, they can calculate a very accurate estimate of the age of the remains. Carbon dating has been a very important tool in building up accurate historical records.

Activity :: Case Study : Using radiocarbon dating

Radiocarbon dating has played an important role in uncovering many aspects of South Africa's history. Read the following extract from an article that appeared in Afrol news on 10th February 2007 and then answer the questions that follow.

The world famous rock art in South Africa's uKhahlamba-Drakensberg, a World Heritage Site, is three times older than previously thought, archaeologists conclude in a new study. The more than 40,000 paintings were made by the San people some 3000 years ago, a new analysis had shown.

Previous work on the age of the rock art in uKhahlamba-Drakensberg concluded it is less than 1,000 years old. But the new study - headed by a South African archaeologist leading a team from the University of Newcastle upon Tyne (UK) and Australian National University in Canberra - estimates the panels were created up to 3,000 years ago. They used the latest radio-carbon dating technology.

The findings, published in the current edition of the academic journal 'South African Humanities', have "major implications for our understanding of how the rock artists lived and the social changes that were taking place over the last three millennia," according to a press release from the British university.

Questions:

- 1. What is the half-life of carbon-14?
- 2. In the news article, what role did radiocarbon dating play in increasing our knowledge of South Africa's history?
- 3. Radiocarbon dating can also be used to analyse the remains of once-living organisms. Imagine that a set of bones are found between layers of sediment and rock in a remote area. A group of archaeologists carries out a series of tests to try to estimate the age of the bones. They calculate that the bones are approximately 23 040 years old.

What percentage of the original carbon-14 must have been left in the bones for them to arrive at this estimate?

7.8 Nuclear Fission

Nuclear fission is a process where the nucleus of an atom is split into two or more smaller nuclei, known as *fission products*. The fission of heavy elements is an **exothermic reaction** and huge amounts of energy are released in the process. This energy can be used to produce *nuclear power* or to make *nuclear weapons*, both of which we will discuss a little later.



Definition: Nuclear fission

The splitting of an atomic nucleus

Below is a diagram showing the nuclear fission of Uranium-235. An atom of Uranium-235 is bombarded with a neutron to initiate the fission process. This neutron is absorbed by Uranium-235, to become Uranium-236. Uranium-236 is highly unstable and breaks down into a number of lighter elements, releasing energy in the process. Free neutrons are also produced during this process, and these are then available to bombard other fissionable elements. This process is known as a **fission chain reaction**, and occurs when one nuclear reaction starts off another, which then also starts off another one so that there is a rapid increase in the number of nuclear reactions that are taking place.



7.8.1 The Atomic bomb - an abuse of nuclear fission

A nuclear chain reaction can happen very quickly, releasing vast amounts of energy in the process. In 1939, it was discovered that Uranium could undergo nuclear fission. In fact, it was uranium that was used in the first atomic bomb. The bomb contained huge amounts of Uranium-235, enough to start a runaway nuclear fission chain reaction. Because the process was uncontrolled, the energy from the fission reactions was released in a matter of *seconds*, resulting in the massive explosion of that first bomb. Since then, more atomic bombs have been dropped, causing massive destruction and loss of life.

Activity :: Discussion : Nuclear weapons testing - an ongoing issue Read the article below which has been adapted from one that appeared in 'The Globe' in Washington on 10th October 2006, and then answer the questions that follow.

US officials and arms control specialists warned yesterday that North Korea's test of a small nuclear device could start an arms race in the region and threaten the landmark global treaty designed nearly four decades ago to halt the spread of nuclear weapons. US officials expressed concern that North Korea's neighbors, including Japan, Taiwan, and South Korea, could eventually decide to develop weapons of their own. They also fear that North Korea's moves could embolden Iran, and that this in turn could encourage Saudi Arabia or other neighbours in the volatile Middle East to one day seek nuclear deterrents, analysts say.

North Korea is the first country to conduct a nuclear test after pulling out of the Nuclear Nonproliferation Treaty. The treaty, which was created in 1968, now includes 185 nations (nearly every country in the world). Under the treaty, the five declared nuclear powers at the time (United States, the Soviet Union, France, China, and Great Britain) agreed to reduce their supplies of nuclear weapons. The treaty has also helped to limit the number of new nuclear weapons nations.

But there have also been serious setbacks. India and Pakistan, which never signed the treaty, became new nuclear powers, shocking the world with test explosions in 1998. The current issue of nuclear weapons testing in North Korea, is another such setback and a blow to the treaty.

Group discussion questions:

1. Discuss what is meant by an 'arms race' and a 'treaty'.

- Do you think it is important to have such treaties in place to control the testing and use of nuclear weapons? Explain your answer.
- 3. Discuss some of the reasons why countries might not agree to be part of a nuclear weapons treaty.
- 4. How would you feel if South Africa decided to develop its own nuclear weapons?

7.8.2 Nuclear power - harnessing energy

However, nuclear fission can also be carried out in a controlled way in a *nuclear reactor*. A nuclear reactor is a piece of equpiment where nuclear chain reactions can be started in a controlled and sustained way. This is different from a nuclear *explosion* where the chain reaction occurs in seconds. The most important use of nuclear reactors at the moment is to produce **electrical power**, and most of these nuclear reactors use nuclear fission. A **nuclear fuel** is a chemical isotope that can keep a fission chain reaction going. The most common isotopes that are used are Uranium-235 and Plutonium-239. The amount of free energy that is in nuclear fuels is far greater than the energy in a similar amount of other fuels such as gasoline. In many countries, nuclear power is seen as a relatively environmentally friendly alternative to fossil fuels, which release large amounts of greenhouse gases, and are also non-renewable resources. However, one of the concerns around the use of nuclear power, is the production of *nuclear waste* which contains radioactive chemical elements.

Activity :: Debate : Nuclear Power

The use of nuclear power as a source of energy has been a subject of much debate. There are many advantages of nuclear power over other energy sources. These include the large amount of energy that can be produced at a small plant, little atmospheric pollution and the small quantity of waste. However there are also disadvantages. These include the expense of maintaining nuclear power stations, the huge impact that an accident could have as well as the disposal of dangerous nuclear waste.

Use these ideas as a starting point for a class debate.

Nuclear power - An energy alternative or environmental hazard?

Your teacher will divide the class into teams. Some of the teams will be 'pro' nuclear power while the others will be 'anti' nuclear power.

7.9 Nuclear Fusion

Nuclear fusion is the joining together of the nuclei of two atoms to form a heavier nucleus. If the atoms involved are small, this process is accompanied by the release of energy. It is the nuclear fusion of elements that causes stars to shine and hydrogen bombs to explode. As with nuclear *fission* then, there are both positive and negative uses of nuclear fusion.



The joining together of the nuclei of two atoms.

You will remember that nuclei naturally repel one another because of the electrostatic force between their positively charged protons. So, in order to bring two nuclei together, a lot of energy must be supplied if fusion is to take place. If two nuclei can be brought close enough together however, the electrostatic force is overwhelmed by the more powerful strong nuclear force which only operates over short distances. If this happens, nuclear fusion can take place. Inside the cores of stars, the temperature is high enough for hydrogen fusion to take place but scientists have so far been unsuccessful in making it work in the laboratory. One of the huge advantages of nuclear fusion, if it could be made to happen, is that it is a relatively environmentally friendly source of energy. The helium that is produced is not radioactive or poisonous and does not carry the dangers of nuclear fission.

7.10 Nucleosynthesis

An astronomer named Edwin Hubble discovered in the 1920's that the universe is expanding. He measured that far-away galaxies are moving away from the earth at great speed, and the further away they are, the faster they are moving.



Extension: What are galaxies?

Galaxies are huge clusters of stars and matter in the universe. The earth is part of the Milky Way galaxy which is shaped like a very large spiral. Astronomers can measure the light coming from distant galaxies using telescopes. Edwin Hubble was also able to measure the velocities of galaxies.

These observations led people to see that the universe is expanding. It also led to the *Big Bang* hypothesis. The 'Big Bang' hypothesis is an idea about how the universe may have started. According to this theory, the universe started off at the beginning of time as a point which then exploded and expanded into the universe we live in today. This happened between 10 and 14 billion years ago.

Just after the Big Bang, when the universe was only 10^{-43} s old, it was very hot and was made up of quarks and leptons (an example of a lepton is the electron). As the universe expanded, ($\sim 10^{-2}$ s) and cooled, the quarks started binding together to form protons and neutrons (together called *nucleons*).

7.10.1 Age of Nucleosynthesis (225 s - 10^3 s)

About 225 s after the Big Bang, the protons and neutrons started binding together to form simple *nuclei*. The process of forming nuclei is called *nucleosynthesis*. When a proton and a neutron bind together, they form the *deuteron*. The deuteron is like a hydrogen nucleus (which is just a proton) with a neutron added to it so it can be written as ²H. Using protons and neutrons as building blocks, more nuclei can be formed as shown below. For example, the Helium-4 nucleus (also called an *alpha particle*) can be formed in the following ways:

 $^{2}H + n \rightarrow ^{3}H$ deuteron + neutron \rightarrow triton

then:

$${}^{3}\text{H} + p \rightarrow {}^{4}\text{He}$$

triton + proton \rightarrow Helium4 (alpha particle)

 $^{2}H + p \rightarrow ^{3}He$ deuteron + proton \rightarrow Helium3 *then:*

 $^{3}\text{He} + n \rightarrow ^{4}\text{He}$ Helium3 + neutron \rightarrow Helium4 (alpha particle)

Some ^{7}Li nuclei could also have been formed by the fusion of ^{4}He and ^{3}H .

7.10.2 Age of lons $(10^3 \text{ s} - 10^{13} \text{ s})$

However, at this time the universe was still very hot and the electrons still had too much energy to become bound to the alpha particles to form helium *atoms*. Also, the nuclei with mass numbers greater than 4 (i.e. greater than ⁴He) are very short-lived and would have decayed almost immediately after being formed. Therefore, the universe moved through a stage called the Age of lons when it consisted of free positively charged $\rm H^+$ ions and ⁴He ions, and negatively charged electrons not yet bound into atoms.

7.10.3 Age of Atoms (10^{13} s - 10^{15} s)

As the universe expanded further, it cooled down until the electrons were able to bind to the hydrogen and helium nuclei to form hydrogen and helium atoms. Earlier, during the Age of lons, both the hydrogen and helium ions were positively charged which meant that they repelled each other (electrostatically). During the Age of Atoms, the hydrogen and helium along with the electrons, were in the form of atoms which are electrically neutral and so they no longer repelled each other and instead pulled together under gravity to form clouds of gas, which evetually formed stars.

7.10.4 Age of Stars and Galaxies (the universe today)

Inside the core of stars, the densities and temperatures are high enough for fusion reactions to occur. Most of the heavier nuclei that exist today were formed inside stars from thermonuclear reactions! (It's interesting to think that the atoms that we are made of were actually manufactured inside stars!). Since stars are mostly composed of hydrogen, the first stage of thermonuclear reactions inside stars involves hydrogen and is called **hydrogen burning**. The process has three steps and results in four hydrogen atoms being formed into a helium atom with (among other things) two photons (light!) being released.

The next stage is **helium burning** which results in the formation of carbon. All these reactions release a large amount of energy and heat the star which causes heavier and heavier nuclei to fuse into nuclei with higher and higher atomic numbers. The process stops with the formation of ⁵⁶Fe, which is the most strongly bound nucleus. To make heavier nuclei, even higher energies are needed than is possible inside normal stars. These nuclei are most likely formed when huge amounts of energy are released, for example when stars explode (an exploding star is called a **supernova**). This is also how all the nuclei formed inside stars get "recycled" in the universe to become part of new stars and planets.

7.11 Summary

• Nuclear physics is the branch of physics that deals with the nucleus of an atom.

- There are two forces between the particles of the nucleus. The **strong nuclear force** is an attractive force between the neutrons and the **electromagnetic force** is the repulsive force between like-charged protons.
- In atoms with large nuclei, the electromagnetic force becomes greater than the strong nuclear force and particles or energy may be released from the nucleus.
- Radioactive decay occurs when an unstable atomic nucleus loses energy by emitting particles or electromagnetic waves.
- The particles and energy released are called **radiation** and the atom is said to be **radioactive**.
- Radioactive isotopes are called radioisotopes.
- Radioactivity was first discovered by Marie Curie and her husband Pierre.
- There are three types of radiation from radioactive decay: **alpha** (α), **beta** (β) and **gamma** (γ) radiation.
- During **alpha decay**, an alpha particle is released. An alpha particle consists of two protons and two neutrons bound together. Alpha radiation has low penetration power.
- During **beta decay**, a beta particle is released. During beta decay, a neutron is converted to a proton, an electron and a neutrino. A beta particle is the electron that is released. Beta radiation has greater penetration power than alpha radiation.
- During **gamma decay**, electromagnetic energy is released as gamma rays. Gamma radiation has the highest penetration power of the three radiation types.
- There are many sources of radiation. Some of natural and others are man-made.
- Natural sources of radiation include cosmic and terrestrial radiation.
- Man-made sources of radiation include televisions, smoke detectors, X-rays and radiation therapy.
- The **half-life** of an element is the time it takes for half the atoms of a radioisotope to decay into other atoms.
- Radiation can be very damaging. Some of the negative impacts of radiation exposure include damage to cells, genetic abnormalities and cancer.
- However, radiation can also have many **positive uses**. These include use in the medical field (e.g. chemical tracers), biochemistry and genetics, use in food preservation, the environment and in archaeology.
- Nuclear fission is the splitting of an atomic nucleus into smaller fission products. Nuclear fission produces large amounts of energy, which can be used to produce nuclear power, and to make nuclear weapons.
- **Nuclear fusion** is the joining together of the nuclei of two atoms to form a heavier nucleus. In stars, fusion reactions involve the joining of hydrogen atoms to form helium atoms.
- **Nucleosynthesis** is the process of forming nuclei. This was very important in helping to form the universe as we know it.



Exercise: Summary exercise

- 1. Explain each of the following terms:
 - (a) electromagnetic force
 - (b) radioactive decay
 - (c) radiocarbon dating

- 2. For each of the following questions, choose the **one correct answer**:
 - (a) The part of the atom that undergoes radioactive decay is the...
 - i. neutrons
 - ii. nucleus
 - iii. electrons
 - iv. entire atom
 - (b) The radio-isotope Po-212 undergoes alpha decay. Which of the following statements is **true**?
 - i. The number of protons in the element remains unchanged.
 - ii. The number of nucleons after decay is 212.
 - iii. The number of protons in the element after decay is 82.
 - iv. The end product after decay is Po-208.
- 3. 20 g of sodium-24 undergoes radoactive decay. Calculate the percentage of the original sample that remains after 60 hours.
- 4. Nuclear physics can be controversial. Many people argue that studying the nucleus has led to devastation and huge loss of life. Others would argue that the benefits of nuclear physics far outweigh the negative things that have come from it.
 - (a) Outline some of the ways in which nuclear physics has been used in negative ways.
 - (b) Outline some of the benefits that have come from nuclear physics.

Chapter 8

Thermal Properties and Ideal Gases - Grade 11

We are surrounded by gases in our atmosphere which support and protect life on this planet. In this chapter, we are going to try to understand more about gases, and learn how to predict how they will behave under different conditions. The kinetic theory of matter was discussed in chapter 2. This theory is very important in understanding how gases behave.

8.1 A review of the kinetic theory of matter

The main assumptions of the kinetic theory of matter are as follows:

- Matter is made up of **particles** (e.g. atoms or molecules)
- These particles are constantly moving because they have kinetic energy. The space in which the particles move is the **volume** of the gas.
- There are **spaces** between the particles
- There are **attractive forces** between particles and these become stronger as the particles move closer together.
- All particles have energy. The temperature of a substance is a measure of the average kinetic energy of the particles.
- A change in **phase** may occur when the energy of the particles is changed.

The kinetic theory applies to all matter, including gases. In a gas, the particles are far apart and have a high kinetic energy. They move around freely, colliding with each other or with the sides of the container if the gas is enclosed. The **pressure** of a gas is a measure of the frequency of collisions of the gas particles with each other and with the sides of the container that they are in. If the gas is heated, the average kinetic energy of the gas particles will increase and if the temperature is decreased, so does their energy. If the energy of the particles decreases significantly, the gas liquifies. An **ideal gas** is one that obeys all the assumptions of the kinetic theory of matter. A **real gas** behaves like an ideal gas, except at high pressures and low temperatures. This will be discussed in more detail later in this chapter.



Definition: Ideal gas

An ideal gas or perfect gas is a hypothetical gas that obeys all the assumptions of the kinetic theory of matter. In other words, an ideal gas would have identical particles of zero volume, with no intermolecular forces between them. The atoms or molecules in an ideal gas would also undergo elastic collisions with the walls of their container.

Definition: Real gas

Real gases behave more or less like ideal gases except under certain conditions e.g. high pressures and low temperatures.

There are a number of laws that describe how gases behave. It will be easy to make sense of these laws if you understand the kinetic theory of gases that was discussed above.

8.2 Boyle's Law: Pressure and volume of an enclosed gas

Activity :: Demonstration : Boyle's Law

If you have ever tried to force in the plunger of a syringe or a bicycle pump while sealing the opening with a finger, you will have seen Boyle's Law in action! This will now be demonstrated using a 10 ml syringe.

Aim:

To demonstrate Boyle's law.

Apparatus:

You will only need a syringe for this demonstration.



Method:

- 1. Hold the syringe in one hand, and with the other pull the plunger out towards you so that the syringe is now full of air.
- 2. Seal the opening of the syringe with your finger so that no air can escape the syringe.
- 3. Slowly push the plunger in, and notice whether it becomes *more* or *less* difficult to push the plunger in.

Results:

What did you notice when you pushed the plunger in? What happens to the **volume** of air inside the syringe? Did it become *more* or *less* difficult to push the plunger in as the volume of the air in the syringe decreased? In other words, did you have to apply more or less **pressure** to the plunger as the volume of air in the syringe decreased?

As the volume of air in the syringe decreases, you have to apply more pressure to the plunger to keep forcing it down. The pressure of the gas inside the syringe pushing back on the plunger is greater. Another way of saying this is that as the volume of the gas in the syringe *decreases*, the pressure of that gas *increases*.

Conclusion:

If the volume of the gas decreases, the pressure of the gas increases. If the volume of the gas increases, the pressure decreases. These results support Boyle's law.

8.2

In the previous demonstration, the volume of the gas decreased when the pressure increased, and the volume increased when the pressure decreased. This is called an **inverse relationship**. The inverse relationship between pressure and volume is shown in figure 8.1.



Figure 8.1: Graph showing the inverse relationship between pressure and volume

Can you use the kinetic theory of gases to explain this inverse relationship between the pressure and volume of a gas? Let's think about it. If you decrease the volume of a gas, this means that the same number of gas particles are now going to come into contact with each other and with the sides of the container much more often. You may remember from earlier that we said that *pressure* is a measure of the *frequency of collisions* of gas particles with each other and with the sides of the container they are in. So, if the volume decreases, the pressure will naturally increase. The opposite is true if the volume of the gas is increased. Now, the gas particles collide less frequently and the pressure will decrease.

It was an Englishman named Robert Boyle who was able to take very accurate measurements of gas pressures and volumes using excellent vacuum pumps. He discovered the startlingly simple fact that the pressure and volume of a gas are not just vaguely inversely related, but are *exactly* **inversely proportional**. This can be seen when a graph of pressure against the inverse of volume is plotted. When the values are plotted, the graph is a straight line. This relationship is shown in figure 8.2.



Figure 8.2: The graph of pressure plotted against the inverse of volume, produces a straight line. This shows that pressure and volume are exactly inversely proportional.



Definition: Boyle's Law

The pressure of a fixed quantity of gas is inversely proportional to the volume it occupies so long as the temperature remains constant.

127

Important: Proportionality

During this chapter, the terms **directly proportional** and **inversely proportional** will be used a lot, and it is important that you understand their meaning. Two quantities are said to be **proportional** if they vary in such a way that one of the quantities is a constant multiple of the other, or if they have a constant ratio. We will look at two examples to show the difference between *directly proportional* and *inversely proportional*.

1. Directly proportional

A car travels at a constant speed of 120 km/h. The time and the distance covered are shown in the table below.

Time (mins)	Distance (km)
10	20
20	40
30	60
40	80

What you will notice is that the two quantities shown are constant multiples of each other. If you divide each distance value by the time the car has been driving, you will always get 2. This shows that the values are proportional to each other. They are **directly proportional** because both values are increasing. In other words, as the driving time increases, so does the distance covered. The same is true if the values decrease. The shorter the driving time, the smaller the distance covered. This relationship can be described mathematically as:

$$y = kx$$

where y is distance, x is time and k is the *proportionality constant*, which in this case is 2. Note that this is the equation for a straight line graph! The symbol \propto is also used to show a directly proportional relationship.

2. Inversely proportional

Two variables are inversely proportional if one of the variables is directly proportional to the multiplicative inverse of the other. In other words,

or

$$y \propto \frac{1}{x}$$
$$y = \frac{k}{x}$$

This means that as one value gets bigger, the other value will get smaller. For example, the time taken for a journey is inversely proportional to the speed of travel. Look at the table below to check this for yourself. For this example, assume that the distance of the journey is 100 km.

Speed (km/h)	Time (mins)	
100	60	
80	75	
60	100	
40	150	

According to our definition, the two variables are inversely proportional is one variable is *directly* proportional to the *inverse* of the other. In other words, if we divide one of the variables by the inverse of the other, we should always get the same number. For example,

$$\frac{100}{1/60} = 6000$$

If you repeat this using the other values, you will find that the answer is always 6000. The variables are inversely proportional to each other.

We know now that the pressure of a gas is *inversely proportional* to the volume of the gas, provided the temperature stays the same. We can write this relationship symbolically as

$$p \propto \frac{1}{V}$$

This equation can also be written as follows:

$$p = \frac{k}{V}$$

where k is a proportionality constant. If we rearrange this equation, we can say that:

pV = k

This equation means that, assuming the temperature is constant, multiplying any pressure and volume values for a fixed amount of gas will always give the same value. So, for example, $p_1V_1 = k$ and $p_2V_2 = k$, where the subscripts 1 and 2 refer to two pairs of pressure and volume readings for the same mass of gas at the same temperature.

From this, we can then say that:

$$p_1V_1 = p_2V_2$$



Important: Remember that Boyle's Law requires two conditions. First, the amount of gas must stay constant. Clearly, if you let a little of the air escape from the container in which it is enclosed, the pressure of the gas will decrease along with the volume, and the inverse proportion relationship is broken. Second, the temperature must stay constant. Cooling or heating matter generally causes it to contract or expand. In our original syringe demonstration, if you were to heat up the gas in the syringe, it would expand and force you to apply a greater force to keep the plunger at a given position. Again, the proportionality would be broken.

the In gas equations, kis a "variable constant". This means that k is constant in a particular set of situations, but in two different sets of situations it has different constant values.

Activity :: Investigation : Boyle's Law

Here are some of Boyle's original data. Note that pressure would originally have been measured using a *mercury manometer* and the units for pressure would have been *millimetres mercury* or mm Hg. However, to make things a bit easier for you, the pressure data have been converted to a unit that is more familiar. Note that the volume is given in terms of arbitrary marks (evenly made).

Volume (graduation mark)	Pressure (kPa)	Volume (graduation mark)	Pressure (kPa)
12	398	28	170
14	340	30	159
16	298	32	150
18	264	34	141
20	239	36	133
22	217	38	125
24	199	40	120
26	184		

1. Plot a graph of pressure (p) against volume (V). Volume will be on the x-axis and pressure on the y-axis. Describe the relationship that you see.

- 2. Plot a graph of p against 1/V. Describe the relationship that you see.
- 3. Do your results support Boyle's Law? Explain your answer.



Did you know that the mechanisms involved in *breathing* also relate to Boyle's Law? Just below the lungs is a muscle called the **diaphragm**. When a person breathes in, the diaphragm moves down and becomes more 'flattened' so that the volume of the lungs can increase. When the lung volume *increases*, the pressure in the lungs *decreases* (Boyle's law). Since air always moves from areas of high pressure to areas of lower pressure, air will now be drawn into the lungs because the air pressure *outside* the body is higher than the pressure *in* the lungs. The opposite process happens when a person breathes out. Now, the diaphragm moves upwards and causes the volume of the lungs to *decrease*. The pressure in the lungs will *increase*, and the air that was in the lungs will be forced out towards the lower air pressure outside the body.



Worked Example 26: Boyle's Law 1

Question: A sample of helium occupies a volume of 160 cm^3 at 100 kPa and 25 °C. What volume will it occupy if the pressure is adjusted to 80 kPa and if the temperature remains unchanged?

Answer

Step 4 : Write down all the information that you know about the gas. $V_1=160\ cm^3$ and $V_2=$? $p_1=100\ kPa$ and $p_2=80\ kPa$

Step 1 : Use an appropriate gas law equation to calculate the unknown variable.

Because the temperature of the gas stays the same, the following equation can be used:

 $p_1V_1 = p_2V_2$

If the equation is rearranged, then

$$V_2 = \frac{p_1 V_1}{p_2}$$

Step 2 : Substitute the known values into the equation, making sure that the units for each variable are the same. Calculate the unknown variable.

$$V_2 = \frac{100 \times 160}{80} = 200 cm^3$$

The volume occupied by the gas at a pressure of 80kPa, is 200 cm³
Worked Example 27: Boyle's Law 2

Question: The pressure on a 2.5 l volume of gas is increased from 695 Pa to 755 Pa while a constant temperature is maintained. What is the volume of the gas under these pressure conditions?

Answer

Step 1 : Write down all the information that you know about the gas. $V_1=2.5$ I and $V_2=$? $p_1=695$ Pa and $p_2=755$ Pa

At constant temperature,

$$p_1V_1 = p_2V_2$$

Therefore,

$$V_2 = \frac{p_1 V_1}{p_2}$$

Step 3 : Substitute the known values into the equation, making sure that the units for each variable are the same. Calculate the unknown variable.

$$V_2 = \frac{695 \times 2.5}{755} = 2.3l$$



Important:

It is not necessary to convert to Standard International (SI) units in the examples we have used above. Changing pressure and volume into different units involves *multiplication*. If you were to change the units in the above equation, this would involve multiplication on both sides of the equation, and so the conversions cancel each other out. However, although SI units don't have to be used, you must make sure that for each variable you use the *same* units throughout the equation. This is not true for some of the calculations we will do at a later stage, where SI units *must* be used.

Exercise: Boyle's Law

- 1. An unknown gas has an initial pressure of 150 kPa and a volume of 1 L. If the volume is increased to 1.5 L, what will the pressure now be?
- 2. A bicycle pump contains 250 cm³ of air at a pressure of 90 kPa. If the air is compressed, the volume is reduced to 200 cm³. What is the pressure of the air inside the pump?
- 3. The air inside a syringe occupies a volume of 10 cm³ and exerts a pressure of 100 kPa. If the end of the syringe is sealed and the plunger is pushed down, the pressure increases to 120 kPa. What is the volume of the air in the syringe?
- 4. During an investigation to find the relationship between the pressure and volume of an enclosed gas at constant temperature, the following results were obtained.

Volume (cm ³)	Pressure (kPa)
40	125.0
30	166.7
25	200.0

- (a) For the results given in the above table, plot a graph of **pressure** (y-axis) against the **inverse of volume** (x-axis).
- (b) From the graph, deduce the relationship between the pressure and volume of an enclosed gas at constant temperature.
- (c) Use the graph to predict what the volume of the gas would be at a pressure of 40 kPa. Show on your graph how you arrived at your answer.

(IEB 2004 Paper 2)

8.3 Charles's Law: Volume and Temperature of an enclosed gas

Charles's law describes the relationship between the **volume** and **temperature** of a gas. The law was first published by Joseph Louis Gay-Lussac in 1802, but he referenced unpublished work by Jacques Charles from around 1787. This law states that at constant pressure, the volume of a given mass of an ideal gas increases or decreases by the same factor as its temperature (in kelvin) increases or decreases. Another way of saying this is that temperature and volume are **directly proportional** (figure **??**).



Definition: Charles's Law

The volume of an enclosed sample of gas is directly proportional to its absolute temperature provided the pressure is kept constant.



Charles's Law is also known as Gay-Lussac's Law. This is because Charles did not publish his discovery, and it was rediscovered independently by another French Chemist Joseph Louis Gay-Lussac some years later.

Activity :: Demonstration : Charles's Law Aim: To demonstrate Charles's Law using simple materials. Apparatus: glass bottle (e.g. empty glass coke bottle), balloon, bunsen burner, retort stand Method:

- 1. Place the balloon over the opening of the empty bottle.
- 2. Place the bottle on the retort stand over the bunsen burner and allow it to heat up. Observe what happens to the balloon. WARNING: Be careful when handling the heated bottle. You may need to wear gloves for protection.

Results:

You should see that the balloon starts to expand. As the air inside the bottle is heated, the pressure also increases, causing the volume to increase. Since the volume of the glass bottle can't increase, the air moves into the balloon, causing it to expand.

Conclusion:

The temperature and volume of the gas are directly related to each other. As one increases, so does the other.

Mathematically, the relationship between temperature and pressure can be represented as follows:

 $V \propto T$ or V = kT

If the equation is rearranged, then...

$$\frac{V}{T} = k$$

and, following the same logic that was used for Boyle's law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

The equation relating volume and temperature produces a straight line graph (refer back to the notes on proportionality if this is unclear). This relationship is shown in figure 8.3.





However, if this graph is plotted on a **celsius** temperature scale, the zero point of temperature doesn't correspond to the zero point of volume. When the volume is zero, the temperature is actually -273.15^{0} C (figure 8.4.

A new temperature scale, the Kelvin scale must be used instead. Since zero on the Celsius scale corresponds with a Kelvin temperature of -273.15° C, it can be said that:

Kelvin temperature
$$(T) = Celsius$$
 temperature $(t) + 273.15$



Figure 8.4: The relationship between volume and temperature, shown on a Celsius temperature scale.

At school level, you can simplify this slightly and convert between the two temperature scales as follows:

$$T = t + 273$$

or
$$t = T - 273$$

Can you explain Charles's law in terms of the kinetic theory of gases? When the temperature of a gas increases, so does the average speed of its molecules. The molecules collide with the walls of the container more often and with greater impact. These collisions will push back the walls, so that the gas occupies a greater volume than it did at the start. We saw this in the first demonstration. Because the glass bottle couldn't expand, the gas pushed out the balloon instead.



Exercise: Charles's law

The table below gives the temperature (in $\,^0\text{C})$ of a number of gases under different volumes at a constant pressure.

Volume (I)	He	H_2	N_2O
0	-272.4	-271.8	-275.0
0.25	-245.5	-192.4	-123.5
0.5	-218.6	-113.1	28.1
0.75	-191.8	-33.7	179.6
1.0	-164.9	45.7	331.1
1.5	-111.1	204.4	634.1
2	-57.4	363.1	937.2
2.5	-3.6	521.8	1240.2
3.0	50.2	680.6	1543.2
3.5	103.9	839.3	1846.2

- 1. On the same set of axes, draw graphs to show the relationship between temperature and volume for each of the gases.
- 2. Describe the relationship you observe.
- 3. If you extrapolate the graphs (in other words, extend the graph line even though you may not have the exact data points), at what temperature do they intersect?
- 4. What is significant about this temperature?



Worked Example 28: Charles's Law 1

Question: Ammonium chloride and calcium hydroxide are allowed to react. The ammonia that is released in the reaction is collected in a gas syringe and sealed in. This gas is allowed to come to room temperature which is 32° C. The volume of the ammonia is found to be 122 ml. It is now placed in a water bath set at 7° C. What will be the volume reading after the syringe has been left in the bath for a good while (assume the plunger moves completely freely)?

Answer

Step 1 : Write down all the information that you know about the gas. $V_1=122$ ml and $V_2=$? $T_1=32^0C$ and $T_2=7^0C$

Step 2 : Convert the known values to SI units if necessary.

Here, temperature must be converted into Kelvin, therefore: T_1 = 32 + 273 = 305 K T_2 = 7 + 273 = 280 K

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Therefore,

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$V_2 = \frac{122 \times 280}{305} = 112ml$$



Important:

Note that here the temperature must be converted to Kelvin (SI) since the change from degrees Celcius involves addition, not multiplication by a fixed conversion ratio (as is the case with pressure and volume.)



Worked Example 29: Charles's Law 2

Question: At a temperature of 298 K, a certain amount of CO_2 gas occupies a volume of 6 l. What volume will the gas occupy if its temperature is reduced to 273 K?

Answer

Step 1 : Write down all the information that you know about the gas. $V_1=6\ I$ and $V_2=?$ $T_1=298\ K$ and $T_2=273\ K$

Step 2 : Convert the known values to SI units if necessary.

Temperature data is already in Kelvin, and so no conversions are necessary.

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Therefore,

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$V_2 = \frac{6 \times 273}{298} = 5.5l$$

8.4 The relationship between temperature and pressure

The pressure of a gas is directly proportional to its temperature, if the volume is kept constant (figure 8.5). When the temperature of a gas increases, so does the energy of the particles. This causes them to move more rapidly and to collide with each other and with the side of the container more often. Since pressure is a measure of these collisions, the pressure of the gas increases with an increase in temperature. The pressure of the gas will decrease if its temperature decreases.



Figure 8.5: The relationship between the temperature and pressure of a gas

In the same way that we have done for the other gas laws, we can describe the relationship between temperature and pressure using symbols, as follows:

$$T \propto p$$
, therefore $p = kT$

We can also say that:

$$\frac{p}{T} = k$$
136

and that, provided the amount of gas stays the same ...

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

?

Exercise: More gas laws

- 1. A gas of unknown volume has a temperature of 14° C. When the temperature of the gas is increased to 100° C, the volume is found to be 5.5 L. What was the initial volume of the gas?
- 2. A gas has an initial volume of 2600 mL and a temperature of 350 K.
 - (a) If the volume is reduced to 1500 mL, what will the temperature of the gas be in Kelvin?
 - (b) Has the temperature increased or decreased?
 - (c) Explain this change, using the kinetic theory of matter.
- 3. A cylinder of propane gas at a temperature of 20°C exerts a pressure of 8 atm. When a cylinder has been placed in sunlight, its temperature increases to 25°C. What is the pressure of the gas inside the cylinder at this temperature?

8.5 The general gas equation

All the gas laws we have described so far rely on the fact that at least one variable (T, p or V) remains constant. Since this is unlikely to be the case most times, it is useful to combine the relationships into one equation. These relationships are as follows:

Boyle's law: $p \propto \frac{1}{V}$ (constant T)

Relationship between p and T: p \propto T (constant V)

If we combine these relationships, we get p $\propto \frac{T}{V}$

If we introduce the proportionality constant k, we get $p = k \frac{T}{V}$

or, rearranging the equation ...

$$pV = kT$$

We can also rewrite this relationship as follows:

$$\frac{pV}{T} = k$$

Provided the mass of the gas stays the same, we can also say that:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

In the above equation, the subscripts 1 and 2 refer to two pressure and volume readings for the same mass of gas under different conditions. This is known as the **general gas equation**.

Temperature is always in kelvin and the units used for pressure and volume must be the same on both sides of the equation.

Important:

Remember that the general gas equation only applies if the mass of the gas is fixed.



Worked Example 30: General Gas Equation 1

Question: At the beginning of a journey, a truck tyre has a volume of 30 dm³ and an internal pressure of 170 kPa. The temperature of the tyre is 16^{0} C. By the end of the trip, the volume of the tyre has increased to 32 dm³ and the temperature of the air inside the tyre is 35^{0} C. What is the tyre pressure at the end of the journey?

Answer

Step 1 : Write down all the information that you know about the gas.

 $\begin{array}{l} \mathsf{p}_1 = 170 \; \mathsf{kPa} \; \mathsf{and} \; \mathsf{p}_2 = ? \\ \mathsf{V}_1 = 30 \; \mathsf{dm}^3 \; \mathsf{and} \; \mathsf{V}_2 = 32 \; \mathsf{dm}^3 \\ \mathsf{T}_1 = 16^0 \mathsf{C} \; \mathsf{and} \; \mathsf{T}_2 = 40^0 \mathsf{C} \end{array}$

Step 2 : Convert the known values to SI units if necessary. Here, temperature must be converted into Kelvin, therefore: T₁ = 16 + 273 = 289 K T₂ = 40 + 273 = 313 K

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

Use the general gas equation to solve this problem:

$$\frac{p_1 \times V_1}{T_1} = \frac{p_2 \times V_2}{T_2}$$

Therefore,

$$p_2 = \frac{p_1 \times V_1 \times T_2}{T_1 \times V_2}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$p_2 = \frac{170 \times 30 \times 313}{289 \times 32} = 173kPa$$

The pressure of the tyre at the end of the journey is 173 kPa.



Worked Example 31: General Gas Equation 2

Question: A cylinder that contains methane gas is kept at a temperature of 15° C and exerts a pressure of 7 atm. If the temperature of the cylinder increases to 25° C, what pressure does the gas now exert? (Refer to table 8.1 to see what an 'atm' is.

Answer Step 1 : Write down all the information that you know about the gas. $p_1=7$ atm and $p_2=?$ $\mathsf{T}_1=\mathsf{15}^0\mathsf{C}$ and $\mathsf{T}_2=\mathsf{25}^0\mathsf{C}$

Step 2 : Convert the known values to SI units if necessary. Here, temperature must be converted into Kelvin, therefore: T₁ = 15 + 273 = 288 K T₂ = 25 + 273 = 298 K

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

Since the volume of the cylinder is constant, we can write:

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Therefore,

$$p_2 = \frac{p_1 \times T_2}{T_1}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$p_2 = \frac{7 \times 298}{288} = 7.24atm$$

The pressure of the gas is 7.24 atm.



Worked Example 32: General Gas Equation 3

Question: A gas container can withstand a pressure of 130 kPa before it will start to leak. Assuming that the volume of the gas in the container stays the same, at what temperature will the container start to leak if the gas exerts a pressure of 100 kPa at 15° C?

Answer

Step 1 : Write down all the information that you know about the gas. $p_1=100~kPa$ and $p_2=130~kPa$ $T_1=15^0C$ and $T_2=?$

Step 2 : Convert the known values to SI units if necessary.

Here, temperature must be converted into Kelvin, therefore: $\mathsf{T}_1=\mathsf{15}+\mathsf{273}=\mathsf{288}\ \mathsf{K}$

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

Since the volume of the container is constant, we can write:

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Therefore,

$$\frac{1}{T_2} = \frac{p_1}{T_1 \times p_2}$$

Therefore,

$$T_2 = \frac{T_1 \times p_2}{p_1}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$T_2 = \frac{288 \times 130}{100} = 374.4K = 101.4^{\circ}C$$

Exercise: The general gas equation

- 1. A closed gas system initially has a volume of 8 L and a temperature of 100° C. The pressure of the gas is unknown. If the temperature of the gas decreases to 50° C, the gas occupies a volume of 5 L. If the pressure of the gas under these conditions is 1.2 atm, what was the initial pressure of the gas?
- 2. A balloon is filled with helium gas at 27°C and a pressure of 1.0 atm. As the balloon rises, the volume of the balloon increases by a factor of 1.6 and the temperature decreases to 15°C. What is the final pressure of the gas (assuming none has escaped)?
- 3. 25 cm³ of gas at 1 atm has a temperature of 20°C. When the gas is compressed to 20 cm³, the temperature of the gas increases to 28°C. Calculate the final pressure of the gas.

8.6 The ideal gas equation

In the early 1800's, Amedeo Avogadro hypothesised that if you have samples of different gases, of the same volume, at a fixed temperature and pressure, then the samples must contain the same number of freely moving particles (i.e. atoms or molecules).



Definition: Avogadro's Law

Equal volumes of gases, at the same temperature and pressure, contain the same number of molecules.

You will remember from an earlier section, that we combined different gas law equations to get one that included temperature, volume and pressure. In this equation, pV = kT, the value of k is different for different masses of gas. If we were to measure the amount of gas in moles, then k = nR, where n is the number of moles of gas and R is the universal gas constant. The value of R is 8.3143 J.K⁻¹, or for most calculations, 8.3 J.K⁻¹. So, if we replace k in the general gas equation, we get the following **ideal gas equation**.

$$pV = nRT$$



Important:

- 1. The value of R is the same for all gases
- 2. All quantities in the equation pV = nRT must be in the same units as the value of R. In other words, SI units must be used throughout the equation.

The following table may help you when you convert to SI units.

?

Table 8.1: Conversion table showing different units of measurement for volume, pressure and temperature.

Variable	Pressure (p)	Volume (V)	moles (n)	universal gas	temperature
					(R)
SI unit	Pascals (Pa)	m ³	mol	$J.mol.K^{-1}$	kelvin (K)
Other units	760 mm Hg	$1 m^3 =$			$K = {}^{0}C +$
and conver-	= 1 atm $=$	1000000 cm 3			273
sions	$101325 \ {\sf Pa} =$	$=$ 1000 dm 3			
	101.325 kPa	= 1000 litres			



Worked Example 33: Ideal gas equation 1

Question: Two moles of oxygen (O_2) gas occupy a volume of 25 dm³ at a temperature of 40⁰C. Calculate the pressure of the gas under these conditions.

Answer Step 1 : Write down all the information that you know about the gas. p=? V = 25 dm^3 n = 2 $T=40^0C$

Step 2 : Convert the known values to SI units if necessary.

$$V = \frac{25}{1000} = 0.025m^3$$
$$T = 40 + 273 = 313K$$

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$pV = nRT$$

Therefore,

$$p = \frac{nRT}{V}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$p = 2 \times 8.3 \times 3130.025 = 207832Pa = 207.8kPa$$



Worked Example 34: Ideal gas equation 2

Question: Carbon dioxide (CO_2) gas is produced as a result of the reaction between calcium carbonate and hydrochloric acid. The gas that is produced is collected in a 20 dm³ container. The pressure of the gas is 105 kPa at a temperature of 20^oC.

What mass of carbon dioxide was produced?

Answer Step 1 : Write down all the information that you know about the gas. p=105~kPa V $=20~dm^3$ T $=20^0C$

Step 2 : Convert the known values to SI units if necessary.

$$p = 105 \times 1000 = 105000 Pa$$
$$T = 20 + 273 = 293K$$
$$V = \frac{20}{1000} = 0.02m^3$$

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$pV = nRT$$

Therefore,

$$n = \frac{pV}{RT}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$n = \frac{105000 \times 0.02}{8.3 \times 293} = 0.86 moles$$

Step 5 : Calculate mass from moles

$$n = \frac{m}{M}$$

Therefore,

 $m = n \times M$

The molar mass of CO_2 is calculated as follows:

$$M = 12 + (2 \times 16) = 44g.mol^{-1}$$

Therefore,

$$m = 0.86 \times 44 = 37.84q$$



Worked Example 35: Ideal gas equation 3

Question: 1 mole of nitrogen (N_2) reacts with hydrogen (H_2) according to the following equation:

$$N_2 + 3H_2 \rightarrow 2NH_3$$
142

The ammonia (NH_3) gas is collected in a separate gas cylinder which has a volume of 25 dm³. The temperature of the gas is 22⁰C. Calculate the pressure of the gas inside the cylinder.

Answer

Step 1 : Write down all the information that you know about the gas. V = 25 dm³ n = 2 (Calculate this by looking at the mole ratio of nitrogen to ammonia, which is 1:2) T = 22^{0} C

Step 2 : Convert the known values to SI units if necessary.

$$V = \frac{25}{1000} = 0.025m^3$$
$$T = 22 + 273 = 295K$$

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$pV = nRT$$

Therefore,

$$p = \frac{nRT}{V}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$p = \frac{2 \times 8.3 \times 295}{0.025} = 195880 Pa = 195.89 kPa$$



Worked Example 36: Ideal gas equation 4

Question: Calculate the number of air particles in a 10 m by 7 m by 2 m classroom on a day when the temperature is 23° C and the air pressure is 98 kPa.

Answer Step 1 : Write down all the information that you know about the gas. V = 10 m \times 7 m \times 2m = 140 m^3 p = 98 kPa T = 23^0C

Step 2 : Convert the known values to SI units if necessary.

$$p = 98 \times 1000 = 98000Pa$$

$$T = 23 + 273 = 296K$$

Step 3 : Choose a relevant gas law equation that will allow you to calculate the unknown variable.

$$pV = nRT$$
143

Therefore,

$$n = \frac{pV}{RT}$$

Step 4 : Substitute the known values into the equation. Calculate the unknown variable.

$$n = \frac{98000 \times 140}{8.3 \times 296} = 5584.5mol$$



Worked Example 37: Applying the gas laws

Question: Most modern cars are equipped with airbags for both the driver and the passenger. An airbag will completely inflate in 0,05 s. This is important because a typical car collision lasts about 0,125 s. The following reaction of sodium azide (a compound found in airbags) is activated by an electrical signal:

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

- 1. Calculate the mass of $N_2(g)$ needed to inflate a sample airbag to a volume of 65 dm³ at 25 °C and 99,3 kPa. Assume the gas temperature remains constant during the reaction.
- 2. In reality the above reaction is exothermic. Describe, in terms of the kinetic molecular theory, how the pressure in the sample airbag will change, if at all, as the gas temperature returns to 25 $^{\circ}$ C.

Answer

Step 1 : Look at the information you have been given, and the information you still need.

Here you are given the volume, temperature and pressure. You are required to work out the mass of N_2 .

Step 2 : Check that all the units are S.I. units

Pressure: $93,3 \times 10^3$ Pa Volume: 65×10^{-3} m³ Temperature: (273 + 25) K Gas Constant: 8,31

Step 3 : Write out the Ideal Gas formula

$$pV = nRT$$

Step 4 : Solve for the required quantity using symbols

$$n = \frac{pV}{RT}$$

Step 5 : Solve by substituting numbers into the equation to solve for 'n'.

$$n = \frac{99,3 \times 10^3 \times 65 \times 10^{-3}}{8,31 \times (273 + 25)}$$

Step 6 : Convert the number of moles to number of grams

 $m = n \times M$ $m = 2,61 \times 28$ m = 73,0g

Step 7 : Theory Question

When the temperature decreases the intensity of collisions with the walls of the airbag and between particles decreases. Therefore pressure decreases.

Exercise: The ideal gas equation

- 1. An unknown gas has pressure, volume and temperature of 0.9 atm, 8 L and 120°C respectively. How many moles of gas are present?
- 2. 6 g of chlorine (Cl₂) occupies a volume of 0.002 m³ at a temperature of 26°C. What is the pressure of the gas under these conditions?
- 3. An average pair of human lungs contains about 3.5 L of air after inhalation and about 3.0 L after exhalation. Assuming that air in your lungs is at 37°C and 1.0 atm, determine the number of moles of air in a typical breath.
- 4. A learner is asked to calculate the answer to the problem below:

Calculate the pressure exerted by 1.5 moles of nitrogen gas in a container with a volume of 20 dm³ at a temperature of 37° C. The learner writes the solution as follows: $V = 20 \text{ dm}^3$

$$p = \frac{nRV}{T}$$

$$=\frac{1.5\times8.3\times20}{310}$$

 $= 0.8 \ \text{kPa}$

- (a) Identify 2 mistakes the learner has made in the calculation.
- (b) Are the units of the final answer correct?
- (c) Rewrite the solution, correcting the mistakes to arrive at the right answer.

8.7 Molar volume of gases

It is possible to calculate the volume of a mole of gas at STP using what we now know about gases.

1. Write down the ideal gas equation

pV = nRT, therefore $V = \frac{nRT}{p}$

- 2. Record the values that you know, making sure that they are in SI units You know that the gas is under STP conditions. These are as follows:
 - p = 101.3 kPa = 101300 Pa
 - $\mathsf{n}=1$ mole
 - $\mathsf{R}=\mathsf{8.3}~\mathsf{J}.\mathsf{K}^{-1}.\mathsf{mol}^{-1}$
 - T = 273 K
- 3. Substitute these values into the original equation.

$$V = \frac{nRT}{p}$$
$$V = \frac{1mol \times 8.3J.K^{-1}.mol^{-1} \times 273K}{101300Pa}$$

4. Calculate the volume of 1 mole of gas under these conditions The volume of 1 mole of gas at STP is 22.4×10^{-3} m³ = 22.4 dm³.

8.8 Ideal gases and non-ideal gas behaviour

In looking at the behaviour of gases to arrive at the Ideal Gas Law, we have limited our examination to a small range of temperature and pressure. Most gases do obey these laws most of the time, and are called **ideal gases**, but there are deviations at **high pressures** and **low temperatures**. So what is happening at these two extremes?

Earlier when we discussed the kinetic theory of gases, we made a number of assumptions about the behaviour of gases. We now need to look at two of these again because they affect how gases behave either when pressures are high or when temperatures are low.

1. Molecules do occupy volume

This means that when pressures are very high and the molecules are compressed, their volume becomes significant. This means that the total volume available for the gas molecules to move is reduced and collisions become more frequent. This causes the pressure of the gas to be *higher* than what would normally have been predicted by Boyle's law (figure 8.6).



Figure 8.6: Gases deviate from ideal gas behaviour at high pressure.

2. Forces of attraction do exist between molecules

At low temperatures, when the speed of the molecules decreases and they move closer together, the intermolecular forces become more apparent. As the attraction between molecules increases, their movement decreases and there are fewer collisions between them. The pressure of the gas at low temperatures is therefore lower than what would have been expected for an ideal gas (figure 8.7. If the temperature is low enough or the pressure high enough, a real gas will **liquify**.



Figure 8.7: Gases deviate from ideal gas behaviour at low temperatures

8.9 Summary

- The **kinetic theory of matter** helps to explain the behaviour of gases under different conditions.
- An ideal gas is one that obeys all the assumptions of the kinetic theory.
- A real gas behaves like an ideal gas, except at high pressures and low temperatures. Under these conditions, the forces between molecules become significant and the gas will liquify.
- Boyle's law states that the pressure of a fixed quantity of gas is inversely proportional to its volume, as long as the temperature stays the same. In other words, pV = k or

$$\mathsf{p}_1\mathsf{V}_1=\mathsf{p}_2\mathsf{V}_2.$$

• **Charles's law** states that the volume of an enclosed sample of gas is directly proportional to its temperature, as long as the pressure stays the same. In other words,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

• The **temperature** of a fixed mass of gas is directly proportional to its pressure, if the volume is constant. In other words,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

 In the above equations, temperature must be written in Kelvin. Temperature in degrees Celsius (temperature = t) can be converted to temperature in Kelvin (temperature = T) using the following equation:

$$T = t + 273$$

147

• Combining Boyle's law and the relationship between the temperature and pressure of a gas, gives the **general gas equation**, which applies as long as the amount of gas remains constant. The general gas equation is pV = kT, or

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

• Because the mass of gas is not always constant, another equation is needed for these situations. The **ideal gas equation** can be written as

$$pV = nRT$$

where n is the number of moles of gas and R is the universal gas constant, which is 8.3 $J.K^{-1}.mol^{-1}$. In this equation, **SI units** must be used. Volume (m³), pressure (Pa) and temperature (K).

• The volume of one mole of gas under STP is 22.4 dm³. This is called the molar gas volume.

s

Exercise: Summary exercise

- 1. For each of the following, say whether the statement is **true** or **false**. If the statement is false, rewrite the statement correctly.
 - (a) Real gases behave like ideal gases, except at low pressures and low temperatures.
 - (b) The volume of a given mass of gas is inversely proportional to the pressure it exerts.
 - (c) The temperature of a fixed mass of gas is directly proportional to its pressure, regardless of the volume of the gas.
- 2. For each of the following multiple choice questions, choose the **one correct answer**.
 - (a) Which one of the following properties of a fixed quantity of a gas must be kept constant during a Boyle's law investigation?
 - i. density
 - ii. pressure
 - iii. temperature
 - iv. volume
 - (IEB 2003 Paper 2)
 - (b) Three containers of EQUAL VOLUME are filled with EQUAL MASSES of helium, nitrogen and carbon dioxide gas respectively. The gases in the three containers are all at the same TEMPERATURE. Which one of the following statements is correct regarding the pressure of the gases?
 - i. All three gases will be at the same pressure
 - ii. The helium will be at the greatest pressure
 - iii. The nitrogen will be at the greatest pressure
 - iv. The carbon dioxide will be at the greatest pressure

(*IEB 2004 Paper 2*)

- (c) One mole of an ideal gas is stored at a temperature T (in Kelvin) in a rigid gas tank. If the average speed of the gas particles is doubled, what is the new Kelvin temperature of the gas?
 - i. 4T
 - ii. 2T
 - iii. √2T

iv. 0.5 T

(*IEB 2002 Paper 2*)

(d) The ideal gas equation is given by $\mathbf{pV} = \mathbf{nRT}$. Which one of the following conditions is true according to Avogadro's hypothesis?

	а	$p \propto 1/V$	(T = constant)	
	b	$V \propto T$	(p = constant)	
	С	$V \propto n$	(p, T = constant)	
d $p \propto T$ (n =		$p\proptoT$	(n = constant)	
	(DoE Exemplar paper 2, 2007)			

- 3. Use your knowledge of the gas laws to explain the following statements.
 - (a) It is dangerous to put an aerosol can near heat.
 - (b) A pressure vessel that is poorly designed and made can be a serious safety hazard (a pressure vessel is a closed, rigi container that is used to hold gases at a pressure that is higher than the normal air pressure).
 - (c) The volume of a car tyre increases after a trip on a hot road.
- 4. Copy the following set of labelled axes and answer the questions that follow:



- (a) On the axes, **using a solid line**, draw the graph that would be obtained for a fixed mass of an ideal gas if the pressure is kept constant.
- (b) If the gradient of the above graph is measured to be 0.008 m³.K⁻¹, calculate the pressure that 0.3 mol of this gas would exert.

(IEB 2002 Paper 2)

- Two gas cylinders, A and B, have a volume of 0.15 m³ and 0.20 m³ respectively. Cylinder A contains 1.25 mol He gas at pressure p and cylinder B contains 2.45 mol He gas at standard pressure. The ratio of the Kelvin temperatures A:B is 1.80:1.00. Calculate the pressure of the gas (in kPa) in cylinder A. (*IEB 2002 Paper 2*)
- 6. A learner investigates the relationship between the Celsius temperature and the pressure of a fixed amount of helium gas in a 500 cm³ closed container. From the results of the investigation, she draws the graph below:



(a) Under the conditions of this investigation, helium gas behaves like an ideal gas. Explain briefly why this is so.

- (b) From the shape of the graph, the learner concludes that the pressure of the helium gas is directly proportional to the Celcius temperature. Is her conclusion correct? Briefly explain your answer.
- (c) Calculate the pressure of the helium gas at 0 $^{\circ}$ C.
- (d) Calculate the mass of helium gas in the container.

(IEB 2003 Paper 2)

- 7. One of the cylinders of a motor car engine, before compression contains 450 cm³ of a mixture of air and petrol in the gaseous phase, at a temperature of 30°C and a pressure of 100 kPa. If the volume of the cylinder after compression decreases to one tenth of the original volume, and the temperature of the gas mixture rises to 140°C, calculate the pressure now exerted by the gas mixture.
- 8. In an experiment to determine the relationship between pressure and temperature of a fixed mass of gas, a group of learners obtained the following results:

Pressure (kPa)	101	120	130.5	138
Temperature (⁰ C)	0	50	80	100
Total gas volume (cm 3)	250	250	250	250

(a) Draw a straight-line graph of pressure (on the dependent, y-axis) versus temperature (on the independent, x-axis) on a piece of graph paper. Plot the points. Give your graph a suitable heading.

A straight-line graph passing through the origin is essential to obtain a mathematical relationship between pressure and temperature.

- (b) Extrapolate (extend) your graph and determine the temperature (in ⁰C) at which the graph will pass through the temperature axis.
- (c) Write down, in words, the relationship between pressure and Kelvin temperature.
- (d) From your graph, determine the pressure (in kPa) at 173 K. Indicate on your graph how you obtained this value.
- (e) How would the gradient of the graph be affected (if at all) if a larger mass of the gas is used? Write down ONLY increases, decreases or stays the same.

(DoE Exemplar Paper 2, 2007)

Chapter 9

Organic Molecules - Grade 12

9.1 What is organic chemistry?

Organic chemistry is the branch of chemistry that deals with **organic molecules**. An organic molecule is one which contains **carbon**, and these molecules can range in size from simple molecules to complex structures containing thousands of atoms! Although the main element in organic compounds is carbon, other elements such as hydrogen (H), oxygen (O), nitrogen (N), sulfur (S) and phosphorus (P) are also common in these molecules.

Until the early nineteenth century, chemists had managed to make many simple compounds in the laboratory, but were still unable to produce the complex molecules that they found in living organisms. It was around this time that a Swedish chemist called **Jons Jakob Berzelius** suggested that compounds found only in living organisms (the organic compounds) should be grouped separately from those found in the non-living world (the inorganic compounds). He also suggested that the laws that governed how organic compounds formed, were different from those for inorganic compounds. From this, the idea developed that there was a 'vital force' in organic compounds. In other words, scientists believed that organic compounds would not follow the normal physical and chemical laws that applied to other inorganic compounds because the very 'force of life' made them different.

This idea of a mystical 'vital force' in organic compounds was weakened when scientists began to manufacture organic compounds in the laboratory from non-living materials. One of the first to do this was **Friedrich Wohler** in 1828, who successfully prepared urea, an organic compound in the urine of animals which, until that point, had only been found in animals. A few years later a student of Wohler's, **Hermann Kolbe**, made the organic compounds are governed by exactly the same laws that apply to inorganic compounds. The properties of organic compounds are not due to a 'vital force' but to the unique properties of the carbon atom itself.

Organic compounds are very important in daily life. They make up a big part of our own bodies, they are in the food we eat and in the clothes we wear. Organic compounds are also used to make products such as medicines, plastics, washing powders, dyes, along with a list of other items.

9.2 Sources of carbon

The main source of the carbon in organic compounds is **carbon dioxide** in the air. Plants use sunlight to convert carbon dioxide into organic compounds through the process of **photosyn**-**thesis**. Plants are therefore able to make their own organic compounds through photosynthesis, while animals feed on plants or plant products so that they gain the organic compounds that they need to survive.

Another important source of carbon is **fossil fuels** such as coal, petroleum and natural gas. This is because fossil fuels are themselves formed from the decaying remains of dead organisms (refer to chapter 21 for more information on fossil fuels).

9.3 Unique properties of carbon

Carbon has a number of unique properties which influence how it behaves and how it bonds with other atoms:

• Carbon has *four valence electrons* which means that each carbon atom can form bonds with four other atoms. Because of this, long *chain structures* can form. These chains can either be *unbranched* (figure 9.1) or *branched* (figure 9.2). Because of the number of bonds that carbon can form with other atoms, organic compounds can be very complex.



Figure 9.1: An unbranched carbon chain



Figure 9.2: A branched carbon chain

• Because of its position on the Periodic Table, most of the bonds that carbon forms with other atoms are *covalent*. Think for example of a C-C bond. The difference in electronegativity between the two atoms is zero, so this is a pure covalent bond. In the case of a C-H bond, the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is so small that C-H bonds are almost purely covalent. The result of this is that most organic compounds are non-polar. This affects some of the properties of organic compounds.

9.4 Representing organic compounds

There are a number of ways to represent organic compounds. It is useful to know all of these so that you can recognise a molecule however it is shown. There are three main ways of representing a compound. We will use the example of a molecule called 2-methylpropane to help explain the difference between each.

9.4.1 Molecular formula

The molecular formula of a compound shows how many atoms of each type are in a molecule. The number of each atom is written as a subscript after the atomic symbol. The molecular formula of 2-methylpropane is:

 $\mathbf{C}_4\mathbf{H}_{10}$

9.4.2 Structural formula

The structural formula of an organic compound shows every bond between every atom in the molecule. Each bond is represented by a line. The structural formula of 2-methylpropane is shown in figure 9.3.



Figure 9.3: The structural formula of 2-methylpropane

9.4.3 Condensed structural formula

When a compound is represented using its condensed structural formula, each carbon atom and the hydrogen atoms that are bonded directly to it are listed as a molecular formula, followed by a similar molecular formula for the neighbouring carbon atom. Branched groups are shown in brackets after the carbon atom to which they are bonded. The condensed structural formula below shows that in 2-methylpropane, there is a branched chain attached to the second carbon atom of the main chain. You can check this by looking at the structural formula in figure **??**.

CH₃CH(CH₃)CH₃



Exercise: Representing organic compounds

(a)

1. For each of the following organic compounds, give the **condensed structural formula** and the **molecular formula**.





- 2. For each of the following, give the **structural formula** and the **molecular formula**.
 - (a) $CH_3CH_2CH_3$
 - (b) CH₃CH₂CH(CH₃)CH₃
 - (c) C_2H_6
- 3. Give two possible structural formulae for the compound with a molecular formula of $\mathsf{C}_4\mathsf{H}_{10}.$

9.5 Isomerism in organic compounds

It is possible for two organic compounds to have the same *molecular formula* but a different *structural formula*. Look for example at the two organic compounds that are shown in figure 9.4.



Figure 9.4: Isomers of a 4-carbon organic compound

If you were to count the number of carbon and hydrogen atoms in each compound, you would find that they are the same. They both have the same molecular formula (C_4H_{10}) , but their structure is different and so are their properties. Such compounds are called **isomers**.



Definition: Isomer

In chemistry, isomers are molecules with the same molecular formula and often with the same kinds of chemical bonds between atoms, but in which the atoms are arranged differently.

?

Column A			Column B							
	CH ₃ CH(CH ₃)OH			$CH_3CH(CH_3)CH_3$						
	Н	Н	Н	Н			Н	Н	CH_3	
н -	— C —	- C -	- C -	- C -	— н	н —	- C —	- C -	— с — н	
	Н	Н	Н	Н			Н	Н	Н	
	CH_3	Н	Н							
н -	— C —	- C -	– C –	– H						
	Н	Н	Н					C_3H	I ₇ OH	

9.6 Functional groups

All organic compounds have a particular bond or group of atoms which we call its **functional group**. This group is important in determining how a compound will react.



Definition: Functional group

In organic chemistry, a functional group is a specific group of atoms within molecules, that are responsible for the characteristic chemical reactions of those molecules. The same functional group will undergo the same or similar chemical reaction(s) regardless of the size of the molecule it is a part of.

In one group of organic compounds called the **hydrocarbons**, the single, double and triple bonds of the alkanes, elkenes and alkynes are examples of functional groups. In another group, the alcohols, an oxygen and a hydrogen atom that are bonded to each other form the functional group for those compounds. All alcohols will contain an oxygen and a hydrogen atom bonded together in some part of the molecule.

Table 9.1 summarises some of the common functional groups. We will look at these in more detail later in this chapter.

9.7 The Hydrocarbons

Let us first look at a group of organic compounds known as the **hydrocarbons**. These molecules only contain carbon and hydrogen. The hydrocarbons that we are going to look at are called **aliphatic compounds**. The aliphatic compounds are divided into *acyclic compounds* (chain structures) and *cyclic compounds* (ring structures). The chain structures are further divided into structures that contain only *single bonds* (alkanes), those that contain *double bonds* (alkenes) and those that contain *triple bonds* (alkynes). Cyclic compounds include structures such as the *benzene ring*. Figure 9.5 summarises the classification of the hydrocarbons.

Hydrocarbons that contain only single bonds are called **saturated** hydrocarbons because each carbon atom is bonded to as many hydrogen atoms as possible. Figure 9.6 shows a molecule of ethane which is a saturated hydrocarbon.

Name of group	Functional group	Example	Diagram
Alkane	— c — c — 	Ethane	н н н — с — н н н
Alkene) c=c	Ethene	
Alkyne	—c≡c—	Ethyne (acetylene)	н—с≡с—н
Halo-alkane	— C — X (X=F,Cl,Br,I)	Chloroethane	н сн ₃
Alcoh <i>ol</i> / alkan <i>ol</i>	— С — ОН 	Ethanol	Н ОН H—С—С—Н Н Н
Carboxylic acid	-COH	ethanoic acid	О СН ₃ — С — СН ₃
Amine	R—N H	Glycine	

Table 9.1: Some functional groups of organic compounds

Hydrocarbons that contain double or triple bonds are called **unsaturated** hydrocarbons because they don't contain as many hydrogen atoms as possible. Figure 9.7 shows a molecule of ethene which is an unsaturated hydrocarbon. If you compare the number of carbon and hydrogen atoms



Figure 9.5: The classification of the aliphatic hydrocarbons



Figure 9.6: A saturated hydrocarbon

in a molecule of ethane and a molecule of ethene, you will see that the number of hydrogen atoms in ethene is *less* than the number of hydrogen atoms in ethane despite the fact that they both contain two carbon atoms. In order for an unsaturated compound to become saturated, a double bond has to be broken, and another two hydrogen atoms added for each double bond that is replaced by a single bond.



Figure 9.7: An unsaturated hydrocarbon



Fat that occurs naturally in living matter such as animals and plants is used as food for human consumption and contains varying proportions of saturated and unsaturated fat. Foods that contain a high proportion of saturated fat are butter, ghee, suet, tallow, lard, coconut oil, cottonseed oil, and palm kernel oil, dairy products (especially cream and cheese), meat, and some prepared foods. Diets high in saturated fat are correlated with an increased incidence of atherosclerosis and coronary heart disease according to a number of studies. Vegetable oils contain unsaturated fats and can be hardened to form margarine by adding hydrogen on to some of the carbon=carbon double bonds using a nickel catalyst. The process is called hydrogenation We will now go on to look at each of the hydrocarbon groups in more detail. These groups are the alkanes, the alkenes and the alkynes.

9.7.1 The Alkanes

The alkanes are hydrocarbons that only contain *single covalent bonds* between their carbon atoms. This means that they are *saturated* compounds and are quite unreactive. The simplest alkane has only one carbon atom and is called **methane**. This molecule is shown in figure 9.8.



Figure 9.8: The structural (a) and molecular formula (b) for methane

The second alkane in the series has two carbon atoms and is called **ethane**. This is shown in figure 9.9.



Figure 9.9: The structural (a) and molecular formula (b) for ethane

The third alkane in the series has three carbon atoms and is called **propane** (Figure 9.10).



Figure 9.10: The structural (a) and molecular formula (b) for propane

When you look at the molecular formula for each of the alkanes, you should notice a pattern developing. For each carbon atom that is added to the molecule, two hydrogen atoms are added. In other words, each molecule differs from the one before it by CH_2 . This is called a *homologous series*. The alkanes have the general formula C_nH_{2n+2} .

The alkanes are the most important source of fuel in the world and are used extensively in the chemical industry. Some are gases (e.g. methane and ethane), while others are liquid fuels (e.g. octane, an important component of petrol).



Some fungi use alkanes as a source of carbon and energy. One fungus *Amorphotheca resinae* prefers the alkanes used in aviation fuel, and this can cause problems for aircraft in tropical areas!

9.7.2 Naming the alkanes

In order to give compounds a name, certain rules must be followed. When naming organic compounds, the IUPAC (International Union of Pure and Applied Chemistry) nomenclature is used. We will first look at some of the steps that need to be followed when naming a compound, and then try to apply these rules to some specific examples.

- 1. STEP 1: Recognise the *functional group* in the compound. This will determine the suffix (the 'end') of the name. For example, if the compound is an alkane, the suffix will be -ane; if the compound is an alkene the suffix will be -ene; if the compound is an alcohol the suffix will be -ol, and so on.
- 2. STEP 2: Find the longest continuous carbon chain (it won't always be a *straight* chain) and count the number of carbon atoms in this chain. This number will determine the prefix (the 'beginning') of the compound's name. These prefixes are shown in table 9.2. So, for example, an alkane that has 3 carbon atoms will have the suffix *prop* and the compound's name will be *propane*.

Carbon atoms	prefix
1	meth(ane)
2	eth(ane)
3	prop(ane)
4	but(ane)
5	pent(ane)
6	hex(ane)
7	hept(ane)
8	oct(ane)
9	non(ane)
10	dec(ane)

Table 9.2: The prefix of a compound's name is determined by the number of carbon atoms in the longest chain

- 3. STEP 3: Number the carbons in the longest carbon chain (Important: If there is a double or triple bond, you need to start numbering so that the bond is at the carbon with the lowest number.
- 4. STEP 4: Look for any branched groups and name them. Also give them a number to show their position on the carbon chain. If there are no branched groups, this step can be left out.
- 5. STEP 5: Combine the elements of the name into a single word in the following order: branched groups; prefix; name ending according to the functional group and its position along the longest carbon chain.



Worked Example 38: Naming the alkanes

Question: Give the IUPAC name for the following compound: Note: The numbers attached to the carbon atoms would not normally be shown. The atoms have been numbered to help you to name the compound.

Answer

Step 1 : Identify the functional group

The compound is a hydrocarbon with single bonds between the carbon atoms. It is an alkane and will have a suffix of -ane.

Step 2 : Find the longest carbon chain



There are four carbon atoms in the longest chain. The prefix of the compound will be 'but'.

Step 3 : Number the carbons in the longest chain In this case, it is easy. The carbons are numbered from left to right, from one to four.

Step 4 : Look for any branched groups, name them and give their position on the carbon chain

There are no branched groups in this compound.

Step 5 : Combine the elements of the name into a single word The name of the compound is **butane**.



Worked Example 39: Naming the alkanes

 $\ensuremath{\textbf{Question:}}$ Give the IUPAC name for the following compound:



Answer Step 1 : Identify the functional group

The compound is an alkane and will have the suffix -ane.

Step 2 : Find the longest carbon chain

There are three carbons in the longest chain. The prefix for this compound is -prop.

Step 3 : Number the carbons in the carbon chain

If we start at the carbon on the left, we can number the atoms as shown below:

Step 4 : Look for any branched groups, name them and give their position on the carbon chain

There is a branched group attached to the second carbon atom. This group has the formula CH_3 which is methane. However, because it is not part of the main chain, it is given the suffix -yl (i.e. methyl). The position of the methyl group comes just



before its name (see next step).

Step 5 : Combine the elements of the compound's name into a single word in the order of branched groups; prefix; name ending according to the functional group.

The compound's name is 2-methylpropane.



Worked Example 40: Naming the alkanes

Question: Give the IUPAC name for the following compound:

 $CH_3CH(CH_3)CH(CH_3)CH_3$

(Remember that the side groups are shown in brackets after the carbon atom to which they are attached.)

Answer

Step 1 : Draw the compound from its condensed structural formula

The structural formula of the compound is:



Step 2 : Identify the functional group The compound is an alkane and will have the suffix -ane.

Step 3 : Find the longest carbon chain

There are four carbons in the longest chain. The prefix for this compound is -but.

Step 4 : Number the carbons in the carbon chain

If we start at the carbon on the left, carbon atoms are numbered as shown in the diagram above. A second way that the carbons could be numbered is:



Step 5 : Look for any branched groups, name them and give their position on the carbon chain

There are two methyl groups attached to the main chain. The first one is attached to the second carbon atom and the second methyl group is attached to the third carbon atom. Notice that in this example it does not matter how you have chosen to number the carbons in the main chain; the methyl groups are still attached to the second and third carbons and so the naming of the compound is not affected.

Step 6 : Combine the elements of the compound's name into a single word in the order of branched groups; prefix; name ending according to the functional group.

The compound's name is **2,3-dimethyl-butane**.



Worked Example 41: Naming the alkanes

Question: Give the IUPAC name for the following compound:



Answer

Step 1 : Identify the functional group

The compound is an alkane and will have the suffix -ane.

Step 2 : Find the longest carbon chain and number the carbons in the longest chain.

There are five carbons in the longest chain if they are numbered as shown below. The prefix for the compound is -pent.



Step 3 : Look for any branched groups, name them and give their position on the carbon chain

There are two methyl groups attached to the main chain. The first one is attached to the first carbon atom and the second methyl group is attached to the third carbon atom.

Step 4 : Combine the elements of the compound's name into a single word in the order of branched groups; prefix; name ending according to the functional group.

The compound's name is **1,3-dimethyl-pentane**.

Exercise: Naming the alkanes

- 1. Give the structural formula for each of the following:
 - (a) Octane
 - (b) $CH_3CH_2CH_3$
 - (c) CH₃CH(CH₃)CH₃
 - (d) 3-ethyl-pentane
- 2. Give the IUPAC name for each of the following organic compounds.



9.7.3 Properties of the alkanes

We have already mentioned that the alkanes are relatively unreactive because of their stable C-C and C-H bonds. The boiling point and melting point of these molecules is determined by their molecular structure, and their surface area. The more carbon atoms there are in an alkane, the greater the surface area and therefore the higher the boiling point. The melting point also increases as the number of carbon atoms in the molecule increases. This can be seen in the data in table 9.3.

Formula	Name	Melting point (⁰ C)	Boiling point (⁰ C)	Phase at room temperature
CH_4	methane	-183	-162	gas
C_2H_6	ethane	-182	-88	gas
C_3H_8	propane	-187	-45	gas
C_4H_{10}	butane	-138	-0.5	gas
C_5H_{12}	pentane	-130	36	liquid
C_6H_{14}	hexane	-95	69	liquid
$C_{17}H_{36}$	heptadecane	22	302	solid

Table 9.3: Properties of some of the alkanes

You will also notice that, when the molecular mass of the alkanes is low (i.e. there are few carbon atoms), the organic compounds are *gases* because the intermolecular forces are weak. As the number of carbon atoms and the molecular mass increases, the compounds are more likely to be liquids or solids because the intermolecular forces are stronger.

9.7.4 Reactions of the alkanes

There are three types of reactions that can occur in saturated compounds such as the alkanes.

1. Substitution reactions

Substitution reactions involve the removal of a hydrogen atom which is replaced by an atom of another element, such as a halogen (F, Cl, Br or I) (figure 9.11). The product is called a **halo-alkane**. Since alkanes are not very reactive, heat or light are needed for this



Figure 9.11: A substitution reaction

reaction to take place.

9.7

e.g. $CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2 - Br$ (halo-alkane)

Halo-alkanes (also sometimes called *alkyl halides*) that contain methane and chlorine are substances that can be used as anaesthetics during operations. One example is trichloromethane, also known as 'chloroform' (figure 9.12).



Figure 9.12: Trichloromethane

2. Elimination reactions

Saturated compounds can also undergo elimination reactions to become unsaturated (figure 9.13). In the example below, an atom of hydrogen and chlorine are eliminated from the original compound to form an unsaturated halo-alkene.

e.g. $CH_2Cl - CH_2Cl \rightarrow CH_2 = CHCl + HCl$



Figure 9.13: An elimination reaction

3. Oxidation reactions

When alkanes are burnt in air, they react with the oxygen in air and heat is produced. This is called an oxidation or combustion reaction. Carbon dioxide and water are given off as products. Heat is also released during the reaction. The burning of alkanes provides most of the energy that is used by man.

e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + heat$

- 1. Give the IUPAC name for each of the following alkanes:
 - (a) C_6H_{14}



- (c) CH_3CH_3
- 2. Give the structural formula for each of the following compounds:
 - (a) octane
 - (b) 3-methyl-hexane
- 3. Methane is one of the simplest alkanes and yet it is an important fuel source. Methane occurs naturally in wetlands, natural gas and permafrost. However, methane can also be produced when organic wastes (e.g. animal manure and decaying material) are broken down by bacteria under conditions that are anaerobic (there is no oxygen). The simplified reaction is shown below:

$\mathsf{Organic}\ \mathsf{matter} \to \mathrm{Simple}\ \mathrm{organic}\ \mathrm{acids} \to \mathrm{Biogas}$

The organic matter could be carbohydrates, proteins or fats which are broken down by acid-forming bacteria into simple organic acids such as acetic acid or formic acid. Methane-forming bacteria then convert these acids into biogases such as methane and ammonia.

The production of methane in this way is very important because methane can be used as a fuel source. One of the advantages of methane over other fuels like coal, is that it produces more energy but with lower carbon dioxide emissions. The problem however, is that methane itself is a greenhouse gas and has a much higher global warming potential than carbon dioxide. So, producing methane may in fact have an even more dangerous impact on the environment.

- (a) What is the structural formula of methane?
- (b) Write an equation to show the reaction that takes place when methane is burned as a fuel.
- (c) Explain what is meant by the statement that methane 'has a greater global warming potential than carbon dioxide'.
- 4. Chlorine and ethane react to form chloroethane and hydrogen chloride.
 - (a) Write a balanced chemical equation for this reaction, using molecular formulae.
 - (b) Give the structural formula of chloroethane.
 - (c) What type of reaction has taken place in this example?
- 5. Petrol (C_8H_{18}) is in fact not pure C_8H_{18} but a mixture of various *alkanes*. The 'octane rating' of petrol refers to the percentage of the petrol which is C_8H_{18} . For example, 93 octane fuel contains 93% C_8H_{18} and 7% other alkanes. The *isomer* of C_8H_{18} referred to in the 'octane rating' is in fact not octane but 2,2,4-trimethylpentane.
 - (a) Write an unbalanced equation for the chemical reaction which takes place when petrol (C_8H_{18}) burns in excess oxygen.
 - (b) Write the general formula of the *alkanes*.
 - (c) Define the term *structural isomer*.
 - (d) Use the information given in this question and your knowledge of naming organic compounds to deduce and draw the full structural formula for 2,2,4-trimethylpentane. (IEB pg 25)

9.7.5 The alkenes

In the alkenes, there is at least one double bond between two carbon atoms. This means that they are **unsaturated** and are *more reactive* than the alkanes. The simplest alkene is ethene (also known as ethylene), which is shown in figure 9.14.



Figure 9.14: The (a) structural, (b) condensed structural and (c) molecular structure representations of ethene

As with the alkanes, the elkenes also form a homologous series. They have the general formula C_nH_{2n} . The second alkene in the series would therefore be C_3H_6 . This molecule is known as propene (figure 9.15). Note that if an alkene has two double bonds, it is called a **diene** and if it has three double bonds it is called a **triene**.



Figure 9.15: The (a) structural, (b) condensed structural and (c) molecular structure representations of propene

The elkenes have a variety of uses. Ethylene for example is a hormone in plants that stimulates the ripening of fruits and the opening of flowers. Propene is an important compound in the petrochemicals industry. It is used as a monomer to make polypropylene and is also used as a fuel gas for other industrial processes.

9.7.6 Naming the alkenes

Similar rules will apply in naming the alkenes, as for the alkanes.



Worked Example 42: Naming the alkenes

Question: Give the IUPAC name for the following compound:


Answer Step 1 : Identify the functional group

The compound is an alkene and will have the suffix -ene.

Step 2 : Find the longest carbon chain

There are four carbon atoms in the longest chain and so the prefix for this compound will be 'but'.

Step 3 : Number the carbon atoms

Remember that when there is a double or triple bond, the carbon atoms must be numbered so that the double or triple bond is at the lowest numbered carbon. In this case, it doesn't matter whether we number the carbons from the left to right, or from the right to left. The double bond will still fall between C_2 and C_3 . The position of the bond will come just before the suffix in the compound's name.

Step 4 : Look for any branched groups, name them and give their position on the carbon chain

There are no branched groups in this molecule.

Step 5 : Name the compound

The name of this compound is **but-2-ene**.



Worked Example 43: Naming the alkenes

Question: Draw the structural formula for the organic compound 3-methyl-butene

Answer

Step 1 : Identify the functional group

The suffix -ene means that this compound is an alkene and there must be a double bond in the molecule. There is no number immediately before the suffix which means that the double bond must be at the first carbon in the chain.

Step 2 : Determine the number of carbons in the longest chain

The prefix for the compound is 'but' so there must be four carbons in the longest chain.

Step 3 : Look for any branched groups

There is a methyl group at the third carbon atom in the chain.

Step 4 : Combine this information to draw the structural formula for this molecule.



Worked Example 44: Naming the alkenes

Question: Give the IUPAC name for the following compound:



Answer

Step 1 : Identify the functional group

The compound is an alkene and will have the suffix -ene. There is a double bond between the first and second carbons and also between the third and forth carbons. The organic compound is therefore a 'diene'.

Step 2 : Find the longest carbon chain and number the carbon atoms

There are four carbon atoms in the longest chain and so the prefix for this compound will be 'but'. The carbon atoms are numbered 1 to 4 in the diagram above. Remember that the main carbon chain must contain both the double bonds.

Step 3 : Look for any branched groups, name them and give their position on the carbon chain

There is a methyl group on the first carbon and an ethyl group on the second carbon.

Step 4 : Name the compound

The name of this compound is 1-methyl,2-ethyl-1,3 diene.



Exercise: Naming the alkenes

Give the IUPAC name for each of the following alkenes:

- 1. C_5H_{10}
- 2. CH₃CHCHCH₃



9.7.7 The properties of the alkenes

The properties of the alkenes are very similar to those of the alkanes, except that the alkenes are more reactive because they are unsaturated. As with the alkanes, compounds that have four or less carbon atoms are gases at room temperature, while those with five or more carbon atoms are liquids.

9.7.8 Reactions of the alkenes

Alkenes can undergo **addition reactions** because they are unsaturated. They readily react with hydrogen, water and the halogens. The double bond is broken and a single, saturated bond is formed. A new group is then added to one or both of the carbon atoms that previously made up the double bond. The following are some examples:

1. Hydrogenation reactions

A catalyst such as platinum is normally needed for these reactions $CH_2=CH_2+H_2 \rightarrow CH_3-CH_3$ (figure 9.16)



Figure 9.16: A hydrogenation reaction

2. Halogenation reactions

 $CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2 - Br$ (figure 9.17)



Figure 9.17: A halogenation reaction

3. The formation of alcohols

 $CH_2 = CH_2 + H_2O \rightarrow CH_3 - CH_2 - OH$ (figure 9.18)



Figure 9.18: The formation of an alcohol

Exercise: The Alkenes

1. Give the IUPAC name for each of the following organic compounds:



2. Refer to the data table below which shows the melting point and boiling point for a number of different organic compounds.

Formula	Name	Melting point (⁰ C)	Boiling point (⁰ C)
C_4H_{10}	Butane	-138	-0.5
C_5H_{12}	Pentane	-130	36
C_6H_{14}	Hexane	-95	69
C_4H_8	Butene	-185	-6
C_5H_{10}	Pentene	-138	30
C_6H_{12}	Hexene	-140	63

- (a) At room temperature (approx. 25^{0} C), which of the organic compounds in the table are:
 - i. gases
 - ii. liquids
- (b) In the alkanes...
 - i. Describe what happens to the melting point and boiling point as the number of carbon atoms in the compound increases.
 - ii. Explain why this is the case.
- (c) If you look at an alkane and an alkene that have the same number of carbon atoms...
 - i. How do their melting points and boiling points compare?
 - ii. Can you explain why their melting points and boiling points are different?
- (d) Which of the compounds, hexane or hexene, is more reactive? Explain your answer.
- 3. The following reaction takes place:

$CH_3CHCH_2 + H_2 \rightarrow CH_3CH_2CH_3$

- (a) Give the name of the organic compound in the reactants.
- (b) What is the name of the product?
- (c) What type of reaction is this?

9.7

(d) Which compound in the reaction is a saturated hydrocarbon?

9.7.9 The Alkynes

In the alkynes, there is at least one triple bond between two of the carbon atoms. They are unsaturated compounds and are therefore highly reactive. Their general formula is C_nH_{2n-2} . The simplest alkyne is ethyne (figure 9.19), also known as acetylene. Many of the alkynes are used to synthesise other chemical products.

н—с≡с—н

Figure 9.19: Ethyne (acetylene)



The raw materials that are needed to make acetylene are calcium carbonate and coal. Acetylene can be produced through the following reactions:

 $CaCO_3 \rightarrow CaO$ $CaO + 3C \rightarrow CaC_2 + CO$ $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

An important use of acetylene is in oxyacetylene gas welding. The fuel gas burns with oxygen in a torch. An incredibly high heat is produced, and this is enough to melt metal.

9.7.10 Naming the alkynes

The same rules will apply as for the alkanes and alkenes, except that the suffix of the name will now be -yne.



Worked Example 45: Naming the alkynes

Question: Give the IUPAC name for the following compound:

$$\begin{array}{rcl} \mathsf{CH}_3 - \mathsf{CH} - \mathsf{CH}_2 - & \mathsf{C} &\equiv & \mathsf{C} & -\mathsf{CH}_3 \\ & & & \\ & & \mathsf{CH}_3 \end{array}$$

Answer Step 1 : Identify the functional group There is a triple bond between two of the carbon atoms, so this compound is an alkyne. The suffix will be -yne. The triple bond is at the second carbon, so the suffix will in fact be 2-yne.

Step 2 : Find the longest carbon chain and give the compound the correct prefix

If we count the carbons in a straight line, there are six. The prefix of the compound's name will be 'hex'.

Step 3 : Number the carbons in the longest chain

In this example, you will need to number the carbons from right to left so that the triple bond is between carbon atoms with the lowest numbers.

Step 4 : Look for any branched groups, name them and show the number of the carbon atom to which the group is attached

There is a methyl (CH_3) group attached to the fifth carbon (remember we have numbered the carbon atoms from right to left).

Step 5 : Combine the elements of the name into a single word in the following order: branched groups; prefix; name ending according to the functional group and its position along the longest carbon chain.

If we follow this order, the name of the compound is 5-methyl-hex-2-yne.

Exercise: The alkynes

Give the IUPAC name for each of the following organic compounds.

H CH₃
| |
H - C - C - C = C - H
| |
H H
1.
2.
$$C_2H_2$$

3. CH_3CH_2CCH

9.8 The Alcohols

An alcohol is any organic compound where there is a *hydroxyl* functional group (-OH) bound to a carbon atom. The general formula for a simple alcohol is $C_nH_{2n+1}OH$.

The simplest and most commonly used alcohols are methanol and ethanol (figure 9.20).

The alcohols have a number of different uses:

- methylated spirits (surgical spirits) is a form of ethanol where methanol has been added
- ethanol is used in alcoholic drinks
- ethanol is used as an industrial solvent



Figure 9.20: (a) methanol and (b) ethanol

- methanol and ethanol can both be used as a fuel and they burn more cleanly than gasoline or diesel (refer to chapter 21 for more information on biofuels as an alternative energy resource.)
- ethanol is used as a solvent in medical drugs, perfumes and vegetable essences
- ethanol is an antiseptic



'Fermentation' refers to the conversion of sugar to alcohol using yeast (a fungus). The process of fermentation produces items such as wine, beer and yoghurt. To make wine, grape juice is fermented to produce alcohol. This reaction is shown below:

 $C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH + energy$



Ethanol is a diuretic. In humans, ethanol reduces the secretion of a hormone called antidiuretic hormone (ADH). The role of ADH is to control the amount of water that the body retains. When this hormone is not secreted in the right quantities, it can cause dehyration because too much water is lost from the body in the urine. This is why people who drink too much alcohol can become dehydrated, and experience symptoms such as headaches, dry mouth, and lethargy. Part of the reason for the headaches is that dehydration causes the brain to shrink away from the skull slightly. The effects of drinking too much alcohol can be reduced by drinking lots of water.

9.8.1 Naming the alcohols

The rules used to name the alcohols are similar to those already discussed for the other compounds, except that the suffix of the name will be different because the compound is an alcohol.





Worked Example 46: Naming alcohols 1

Question: Give the IUPAC name for the following organic compound **Answer**

Step 1 : Identify the functional group

The compound has an -OH (hydroxyl) functional group and is therefore an alcohol. The compound will have the suffix -ol.

Step 2 : Find the longest carbon chain

There are three carbons in the longest chain. The prefix for this compound will be 'prop'. Since there are only single bonds between the carbon atoms, the suffix becomes 'propan' (similar to the alkane 'propane').

Step 3 : Number the carbons in the carbon chain

In this case, it doesn't matter whether you start numbering from the left or right. The hydroxyl group will still be attached to the middle carbon atom, numbered '2'.

Step 4 : Look for any branched groups, name them and give their position on the carbon chain.

There are no branched groups in this compound, but you still need to indicate the position of the hydroxyl group on the second carbon. The suffix will be -2-ol because the hydroxyl group is attached to the second carbon.

Step 5 : Combine the elements of the compound's name into a single word in the order of branched groups; prefix; name ending according to the functional group.

The compound's name is propan-2-ol.



Worked Example 47: Naming alcohols 2

Question: Give the IUPAC name for the following compound:



Answer

Step 1 : Identify the functional group

The compound has an -OH (hydroxyl) functional group and is therefore an alcohol. There are *two* hydroxyl groups in the compound, so the suffix will be -diol.

Step 2 : Find the longest carbon chain

There are four carbons in the longest chain. The prefix for this compound will be 'butan'.

Step 3 : Number the carbons in the carbon chain

The carbons will be numbered from left to right so that the two hydroxyl groups are attached to carbon atoms with the lowest numbers.

Step 4 : Look for any branched groups, name them and give their position on the carbon chain.

There are no branched groups in this compound, but you still need to indicate the position of the hydroxyl groups on the first and second carbon atoms. The suffix will therefore become 1,2-diol.

Step 5 : Combine the elements of the compound's name into a single word in the order of branched groups; prefix; name ending according to the functional group.

The compound's name is butan-1,2-diol.

Exercise: Naming the alcohols

- 1. Give the structural formula of each of the following organic compounds:
 - (a) pentan-3-ol
 - (b) butan-2,3-diol
 - (c) 2-methyl-propanol
- 2. Give the IUPAC name for each of the following:
 - (a) $CH_3CH_2CH(OH)CH_3$

9.8.2 Physical and chemical properties of the alcohols

The hydroxyl group affects the **solubility** of the alcohols. The hydroxyl group generally makes the alcohol molecule *polar* and therefore more likely to be **soluble** in water. However, the carbon chain resists solubility, so there are two opposing trends in the alcohols. Alcohols with shorter carbon chains are usually more soluble than those with longer carbon chains.

Alcohols tend to have higher **boiling points** than the hydrocarbons because of the strong hydrogen bond between hydrogen and oxygen atoms. Alcohols can show either **acidic** or **basic** properties because of the hydroxyl group. They also undergo oxidation reactions to form aldehydes, ketones and carboxylic acids.

Activity :: Case Study : The uses of the alcohols

Read the extract below and then answer the questions that follow:

The alcohols are a very important group of organic compounds, and they have a variety of uses. Our most common use of the word 'alcohol' is with reference to alcoholic drinks. The alcohol in drinks is in fact **ethanol**. But ethanol has many more uses apart from alcoholic drinks! When ethanol burns in air, it produces carbon dioxide, water and energy and can therefore be used as a fuel on its own, or in mixtures with petrol. Because ethanol can be produced through fermentation, this is a useful way for countries without an oil industry to reduce imports of petrol. Ethanol is also used as a solvent in many perfumes and cosmetics.

Methanol can also be used as a fuel, or as a petrol additive to improve combustion. Most methanol is used as an industrial feedstock, in other words it is used to make other things such as methanal (formaldehyde), ethanoic acid and methyl esters. In most cases, these are then turned into other products.

Propan-2-ol is another important alcohol, which is used in a variety of applications as a solvent.

Questions

- 1. Give the structural formula for propan-2-ol.
- 2. Write a balanced chemical equation for the combustion reaction of ethanol.
- 3. Explain why the alcohols are good solvents.

9.9 Carboxylic Acids

Carboxylic acids are organic acids that are characterised by having a carboxyl group, which has the formula -(C=O)-OH, or more commonly written as -COOH. In a carboxyl group, an oxygen atom is double-bonded to a carbon atom, which is also bonded to a hydroxyl group. The simplest carboxylic acid, methanoic acid, is shown in figure 9.21.



Figure 9.21: Methanoic acid

Carboxylic acids are widespread in nature. Methanoic acid (also known as *formic acid*) has the formula HCOOH and is found in insect stings. Ethanoic acid (CH₃COOH), or *acetic acid*, is the main component of vinegar. More complex organic acids also have a variety of different functions. Benzoic acid (C₆H₅COOH) for example, is used as a food preservative.



A certain type of ant, called formicine ants, manufacture and secrete formic acid, which is used to defend themselves against other organisms that might try to eat them.

9.9.1 Physical Properties

Carboxylic acids are **weak acids**, in other words they only dissociate partially. Why does the carboxyl group have acidic properties? In the carboxyl group, the hydrogen tends to separate itself from the oxygen atom. In other words, the carboxyl group becomes a source of positively-charged hydrogen ions (H^+) . This is shown in figure 9.22.



Figure 9.22: The dissociation of a carboxylic acid

Exercise: Carboxylic acids

1. Refer to the table below which gives information about a number of carboxylic acids, and then answer the questions that follow.

Formula	Common	Source	IUPAC	melting	boiling
	name		name	point	point
				$({}^{0}C)$	$({}^{0}C)$
	formic	ants	methanoi	: 8.4	101
	acid		acid		
CH_3CO_2H		vinegar	ethanoic	16.6	118
			acid		
	propionic	milk	propanoic	-20.8	141
	acid		acid		
$CH_3(CH_2)_2CO_2H$	butyric	butter		-5.5	164
	acid				
	valeric	valerian	pentanoic	-34.5	186
	acid	root	acid		
$CH_3(CH_2)_4CO_2H$	caproic	goats		-4	205
	acid				
	enanthic	vines		-7.5	223
	acid				
$CH_3(CH_2)_6CO_2H$	caprylic	goats		16.3	239
	acid				

- (a) Fill in the missing spaces in the table by writing the formula, common name or IUPAC name.
- (b) Draw the structural formula for butyric acid.
- (c) Give the molecular formula for caprylic acid.
- (d) Draw a graph to show the relationship between molecular mass (on the x-axis) and boiling point (on the y-axis)

9.9

i. Describe the trend you see.

ii. Suggest a reason for this trend.

9.9.2 Derivatives of carboxylic acids: The esters

When an alcohol reacts with a carboxylic acid, an **ester** is formed. Most esters have a characteristic and pleasant smell. In the reaction, the hydrogen atom from the hydroxyl group, and an OH from the carboxlic acid, form a molecule of water. A new bond is formed between what remains of the alcohol and acid. The name of the ester is a combination of the names of the alcohol and carboxylic acid. The suffix for an ester is -oate. An example is shown in figure 9.23.



Figure 9.23: The formation of an ester from an alcohol and carboxylic acid

9.10 The Amino Group

The amino group has the formula $-NH_2$ and consists of a nitrogen atom that is bonded to two hydrogen atoms, and to the carbon skeleton. Organic compounds that contain this functional group are called **amines**. One example is *glycine*. Glycine belongs to a group of organic compounds called *amino acids*, which are the building blocks of proteins.



Figure 9.24: A molecule of glycine

9.11 The Carbonyl Group

The carbonyl group (-CO) consists of a carbon atom that is joined to an oxygen by a double bond. If the functional group is on the *end* of the carbon chain, the organic compound is called a **ketone**. The simplest ketone is *acetone*, which contains three carbon atoms. A ketone has the ending 'one' in its IUPAC name.

Exercise: Carboxylic acids, esters, amines and ketones

1. Look at the list of organic compounds in the table below:

Organic compound	Type of compound
$CH_3CH_2CH_2COOH$	
NH ₂ CH ₂ COOH	
propyl ethanoate	
CH ₃ CHO	

- (a) Complete the table by identifying each compound as either a carboxylic acid, ester, amine or ketone.
- (b) Give the name of the compounds that have been written as condensed structural formulae.
- 2. A chemical reaction takes place and ethyl methanoate is formed.
 - (a) What type of organic compound is ethyl methanoate?
 - (b) Name the two reactants in this chemical reaction.
 - (c) Give the structural formula of ethyl methanoate.

9.12 Summary

- Organic chemistry is the branch of chemistry that deals with organic molecules. An organic molecule is one that contains carbon.
- All **living organisms** contain carbon. Plants use sunlight to convert carbon dioxide in the air into organic compounds through the process of **photosynthesis**. Animals and other organisms then feed on plants to obtain their own organic compounds. **Fossil fuels** are another important source of carbon.
- It is the **unique properties of the carbon atom** that give organic compounds certain properties.
- The carbon atom has **four valence electrons**, so it can bond with many other atoms, often resulting in long chain structures. It also forms mostly **covalent bonds** with the atoms that it bonds to, meaning that most organic molecules are **non-polar**.
- An organic compound can be represented in different ways, using its molecular formula, structural formula or condensed structural formula.
- If two compounds are isomers, it means that they have the same molecular formulae but different structural formulae.
- A functional group is a particular group of atoms within a molecule, which give it certain reaction characteristics. Organic compounds can be grouped according to their functional group.
- The **hydrocarbons** are organic compounds that contain only carbon and hydrogen. They can be further divided into the alkanes, alkenes and alkynes, based on the type of bonds between the carbon atoms.
- The alkanes have only single bonds between their carbon atoms and are unreactive.
- The **alkenes** have at least one **double bond** between two of their carbon atoms. They are more reactive than the alkanes.
- The **alkynes** have at least one **triple bond** between two of their carbon atoms. They are the most reactive of the three groups.
- A hydrocarbon is said to be **saturated** if it contains the maximum possible number of hydrogen atoms for that molecule. The alkanes are all saturated compounds.

9.12

- A hydrocarbon is **unsaturated** if it does not contain the maximum number of hydrogen atoms for that molecule. The alkenes and alkynes are examples of unsaturated molecules. If a double or triple bond is broken, more hydrogen atoms can be added to the molecule.
- There are three types of reactions that occur in the alkanes: **substitution**, **elimination** and **oxidation** reactions.
- The alkenes undergo addition reactions because they are unsaturated.
- Organic compounds are **named** according to their functional group and its position in the molecule, the number of carbon atoms in the molecule and the position of any double and triple bonds. The IUPAC rules for nomenclature are used in the naming of organic molecules.
- Many of the **properties** of the hydrocarbons are determined by their **molecular structure**, the **bonds** between atoms and molecules, and their **surface area**.
- The **melting point** and **boiling point** of the hydrocarbons increases as their number of carbon atoms increases.
- The **molecular mass** of the hydrocarbons determines whether they will be in the gaseous, liquid or solid phase at certain temperatures.
- An alcohol is an organic compound that contains a hydroxyl group (OH).
- The alcohols have a number of different uses including their use as a solvent, for medicinal purposes and in alcoholic drinks.
- The alcohols share a number of **properties** because of the hydroxyl group. The hydroxyl group affects the **solubility** of the alcohols. Those with shorter carbon chains are generally more soluble, and those with longer chains are less soluble. The strong hydrogen bond between the hydrogen and oxygen atoms in the hydroxyl group gives alcohols a higher melting point and boiling point than other organic compounds. The hydroxyl group also gives the alcohols both acidic and basic properties.
- The **carboxylic acids** are organic acids that contain a **carboxyl group** with the formula COOH. In a carboxyl group, an oxygen atom is double-bonded to a carbon atom, which is also bonded to a hydroxyl group.
- The carboxylic acids have weak **acidic properties** because the hydrogen atom is able to dissociate from the carboxyl group.
- An ester is formed when an alcohol reacts with a carboxylic acid.
- The **amines** are organic compounds that contain an **amino** functional group, which has the formula NH₂. Some amines belong to the **amino acid** group, which are the building blocks of proteins.
- The **ketones** are a group of compounds that contain a **carbonyl group**, which consists of an oxygen atom that is double-bonded to a carbon atom. In a ketone, the carbonyl group is on the end of the carbon chain.

Exercise: Summary exercise

- 1. Give **one word** for each of the following descriptions:
 - (a) The group of hydrocarbons to which 2-methyl-propene belongs.
 - (b) The name of the functional group that gives alcohols their properties.
 - (c) The group of organic compounds that have acidic properties.
 - (d) The name of the organic compound that is found in vinegar.
 - (e) The name of the organic compound that is found in alcoholic beverages.

- In each of the following questions, choose the one correct answer from the list provided.
 - (a) When 1-propanol is oxidised by acidified potassium permanganate, the possible product formed is...
 - i. propane
 - ii. propanoic acid
 - iii. methyl propanol
 - iv. propyl methanoate
 - (IEB 2004)
 - (b) What is the IUPAC name for the compound represented by the following structural formula?



- i. 1,2,2-trichlorobutane
- ii. 1-chloro-2,2-dichlorobutane
- iii. 1,2,2-trichloro-3-methylpropane
- iv. 1-chloro-2,2-dichloro-3-methylpropane

(IEB 2003)

- 3. Write balanced equations for the following reactions:
 - (a) Ethene reacts with bromine
 - (b) Ethyne gas burns in an excess of oxygen
 - (c) Ethanoic acid ionises in water
- 4. The table below gives the boiling point of ten organic compounds.

	Compound	Formula	Boiling Point (⁰ C)
1	methane	CH_4	-164
2	ethane	C_2H_6	-88
3	propane	C_3H_8	-42
4	butane	C_4H_{10}	0
5	pentane	C_5H_{12}	36
6	methanol	CH ₃ OH	65
7	ethanol	C_2H_5OH	78
8	propan-1-ol	C ₃ H ₇ OH	98
9	propan-1,2-diol	CH ₃ CHOHCH ₂ OH	189
10	propan-1,2,3-triol	CH ₂ OHCHOHCH ₂ OH	290

The following questions refer to the compounds shown in the above table.

- (a) To which homologous series do the following compounds belong?
 - i. Compounds 1,2 and 3
 - ii. Compounds 6,7 and 8
- (b) Which of the above compounds are gases at room temperature?
- (c) What causes the trend of increasing boiling points of compounds 1 to 5?
- (d) Despite the fact that the length of the carbon chain in compounds 8,9 and 10 is the same, the boiling point of propan-1,2,3-triol is much higher than the boiling point of propan-1-ol. What is responsible for this large difference in boiling point?
- (e) Give the IUPAC name and the structural formula of an isomer of butane.

- (f) Which **one** of the above substances is used as a reactant in the preparation of the ester ethylmethanoate?
- (g) Using structural formulae, write an equation for the reaction which produces ethylmethanoate.

(*IEB 2004*)

5. Refer to the numbered diagrams below and then answer the questions that follow.





- (a) Which one of the above compounds is produced from the fermentation of starches and sugars in plant matter?
 - i. compound 1
 - ii. compound 2
 - iii. compound 3
 - iv. compound 4
- (b) To which one of the following homologous series does compound 1 belong?
 - i. esters
 - ii. alcohols
 - iii. aldehydes
 - iv. carboxylic acids
- (c) The correct IUPAC name for compound 3 is...
 - i. 1,1-dibromo-3-butyne
 - ii. 4,4-dibromo-1-butyne
 - iii. 2,4-dibromo-1-butyne
 - iv. 4,4-dibromo-1-propyne
- (d) What is the correct IUPAC name for compound 4?
 - i. propanoic acid
 - ii. ethylmethanoate
 - iii. methylethanoate
 - iv. methylpropanoate

IEB 2005

- 6. Answer the following questions:
 - (a) What is a homologous series?
 - (b) A mixture of ethanoic acid and methanol is warmed in the presence of concentrated sulphuric acid.
 - i. Using structural formulae, give an equation for the reaction which takes place.

- ii. What is the IUPAC name of the organic compound formed in this reaction?
- (c) Consider the following unsaturated hydrocarbon:



- i. Give the IUPAC name for this compound.
- ii. Give the balanced equation for the combustion of this compound in excess oxygen.

(IEB Paper 2, 2003)

7. Consider the organic compounds labelled A to E.

- A. CH₃CH₂CH₂CH₂CH₂CH₃
- B. C_6H_6
- C. CH₃-Cl
- D. Methylamine н

$$H - C - H$$

$$H - C - C - C - C - C - H$$

$$H - C - C - C - C - C - H$$

$$H - C - H$$

- (a) Write a balanced chemical equation for the preparation of compound C using an alkane as one of the reactants.
- (b) Write down the IUPAC name for compound E.
- (c) Write down the structural formula of an isomer of compound A that has only FOUR carbon atoms in the longest chain.
- (d) Write down the structural formula for compound B.

Chapter 10

Organic Macromolecules - Grade 12

As its name suggests, a macromolecule is a large molecule that forms when lots of smaller molecules are joined together. In this chapter, we will be taking a closer look at the structure and properties of different macromolecules, and at how they form.

10.1 Polymers

Some macromolecules are made up of lots of repeating structural units called **monomers**. To put it more simply, a monomer is like a building block. When lots of similar monomers are joined together by covalent bonds, they form a **polymer**. In an **organic polymer**, the monomers would be joined by the *carbon* atoms of the polymer 'backbone'. A polymer can also be **inorganic**, in which case there may be atoms such as *silicon* in the place of carbon atoms. The key feature that makes a polymer different from other macromolecules, is the repetition of identical or similar monomers in the polymer chain. The examples shown below will help to make these concepts clearer.



Definition: Polymer

Polymer is a term used to describe large molecules consisting of repeating structural units, or monomers, connected by covalent chemical bonds.

1. Polyethene

Chapter 9 looked at the structure of a group of hydrocarbons called the *alkenes*. One example is the molecule **ethene**. The structural formula of ethene is is shown in figure 10.1. When lots of ethene molecules bond together, a polymer called **polyethene** is formed. Ethene is the *monomer* which, when joined to other ethene molecules, forms the *polymer* **polyethene**. Polyethene is a cheap plastic that is used to make plastic bags and bottles.



Figure 10.1: (a) Ethene monomer and (b) polyethene polymer

A polymer may be a chain of thousands of monomers, and so it is impossible to draw the entire polymer. Rather, the structure of a polymer can be condensed and represented as shown in figure 10.2. The monomer is enclosed in brackets and the 'n' represents the number of ethene molecules in the polymer, where 'n' is any whole number. What this shows is that the ethene monomer is repeated an indefinite number of times in a molecule of polyethene.



Figure 10.2: A simplified representation of a polyethene molecule

2. Polypropene

Another example of a polymer is *polypropene* (fig 10.3). Polypropene is also a plastic, but is stronger than polyethene and is used to make crates, fibres and ropes. In this polymer, the monomer is the alkene called **propene**.



Figure 10.3: (a) Propene monomer and (b) polypropene polymer

10.2 How do polymers form?

Polymers are formed through a process called **polymerisation**, where monomer molecules react together to form a polymer chain. Two types of polymerisation reactions are **addition polymerisation** and **condensation polymerisation**.



Definition: Polymerisation

In chemistry, polymerisation is a process of bonding monomers, or *single units* together through a variety of reaction mechanisms to form longer chains called polymers.

10.2.1 Addition polymerisation

In this type of reaction, monomer molecules are added to a growing polymer chain one at a time. No small molecules are eliminated in the process. An example of this type of reaction is the formation of *polyethene* from *ethene* (fig 10.1). When molecules of ethene are joined to each other, the only thing that changes is that the double bond between the carbon atoms in each ethene monomer is replaced by a single bond so that a new carbon-carbon bond can be formed with the next monomer in the chain. In other words, the monomer is an *unsaturated* compound which, after an addition reaction, becomes a *saturated* compound.



There are three stages in the process of addition polymerisation. **Initiation** refers to a chemical reaction that triggers off another reaction. In other words, initiation is the starting point of the polymerisation reaction. **Chain propagation** is the part where monomers are continually added to form a longer and longer polymer chain. During chain propagation, it is the reactive end groups of the polymer chain that react in each propagation step, to add a new monomer to the chain. Once a monomer has been added, the reactive part of the polymer is now in this last monomer unit so that propagation will continue. **Termination** refers to a chemical reaction that destroys the reactive part of the polymer chain so that propagation stops.



Worked Example 48: Polymerisation reactions

Question: A polymerisation reaction takes place and the following polymer is formed:



Note: W, X, Y and Z could represent a number of different atoms or combinations of atoms e.g. H, F, Cl or CH_3 .

- 1. Give the structural formula of the monomer of this polymer.
- 2. To what group of organic compounds does this monomer belong?
- 3. What type of polymerisation reaction has taken place to join these monomers to form the polymer?

Answer

Step $1: \mbox{Look}$ at the structure of the repeating unit in the polymer to determine the monomer.

The monomer is:

$$\begin{matrix} W & X \\ I & I \\ c = c \\ I & I \\ Y & z \end{matrix}$$

Step 2 : Look at the atoms and bonds in the monomer to determine which group of organic compounds it belongs to.

The monomer has a double bond between two carbon atoms. The monomer must be an alkene.

Step 3 : Determine the type of polymerisation reaction.

In this example, unsaturated monomers combine to form a saturated polymer. No atoms are lost or gained for the bonds between monomers to form. They are simply added to each other. This is an addition reaction.

10.2.2 Condensation polymerisation

In this type of reaction, two monomer molecules form a covalent bond and a small molecule such as water is lost in the bonding process. Nearly all biological reactions are of this type. **Polyester** and **nylon** are examples of polymers that form through condensation polymerisation.

1. Polyester

Polyesters are a group of polymers that contain the **ester** functional group in their main chain. Although there are many forms of polyesters, the term *polyester* usually refers to polyethylene terephthalate (PET). PET is made from ethylene glycol (an alcohol) and terephthalic acid (an acid). In the reaction, a hydrogen atom is lost from the alcohol, and a hydroxyl group is lost from the carboxylic acid. Together these form one water molecule which is lost during condensation reactions. A new bond is formed between an oxygen and a carbon atom. This bond is called an **ester linkage**. The reaction is shown in figure 10.4.



Figure 10.4: An acid and an alcohol monomer react (a) to form a molecule of the polyester 'polyethylene terephthalate' (b).

Polyesters have a number of characteristics which make them very useful. They are resistant to stretching and shrinking, they are easily washed and dry quickly, and they are resistant to mildew. It is for these reasons that polyesters are being used more and more in **textiles**. Polyesters are stretched out into fibres and can then be made into fabric and articles of clothing. In the home, polyesters are used to make clothing, carpets, curtains, sheets, pillows and upholstery.



Polyester is not just a textile. Polyethylene terephthalate is in fact a plastic which can also be used to make plastic drink bottles. Many drink bottles are recycled by being reheated and turned into polyester fibres. This type of recycling helps to reduce disposal problems.

2. Nylon

Nylon was the first polymer to be commercially successful. Nylon replaced silk, and was used to make parachutes during World War 2. Nylon is very strong and resistant, and is used in fishing line, shoes, toothbrush bristles, guitar strings and machine parts to name

just a few. Nylon is formed from the reaction of an amine (1,6-diaminohexane) and an acid monomer (adipic acid) (figure 10.5). The bond that forms between the two monomers is called an **amide linkage**. An amide linkage forms between a nitrogen atom in the amine monomer and the carbonyl group in the carboxylic acid.



Figure 10.5: An amine and an acid monomer (a) combine to form a section of a nylon polymer (b).

Int Fac

Nylon was first introduced around 1939 and was in high demand to make stockings. However, as World War 2 progressed, nylon was used more and more to make parachutes, and so stockings became more difficult to buy. After the war, when manufacturers were able to shift their focus from parachutes back to stockings, a number of riots took place as women queued to get stockings. In one of the worst disturbances, 40 000 women queued up for 13 000 pairs of stockings, which led to fights breaking out!

Exercise: Polymers

1. The following monomer is a reactant in a polymerisation reaction:

```
\begin{array}{ccc} H & CH_3 \\ | & | \\ C = C \\ | & | \\ H & CH_3 \end{array}
```

- (a) What is the IUPAC name of this monomer?
- (b) Give the structural formula of the polymer that is formed in this polymerisation reaction.
- (c) Is the reaction an addition or condensation reaction?

2. The polymer below is the product of a polymerisation reaction.



- (a) Give the structural formula of the monomer in this polymer.
- (b) What is the name of the monomer?
- (c) Draw the abbreviated structural formula for the polymer.
- (d) Has this polymer been formed through an addition or condensation polymerisation reaction?
- 3. A condensation reaction takes place between methanol and methanoic acid.
 - (a) Give the structural formula for...
 - i. methanol
 - ii. methanoic acid
 - iii. the product of the reaction
 - (b) What is the name of the product? (Hint: The product is an ester)

10.3 The chemical properties of polymers

The attractive forces between polymer chains play a large part in determining a polymer's properties. Because polymer chains are so long, these interchain forces are very important. It is usually the side groups on the polymer that determine what types of intermolecular forces will exist. The greater the strength of the intermolecular forces, the greater will be the tensile strength and melting point of the polymer. Below are some examples:

• Hydrogen bonds between adjacent chains

Polymers that contain amide or carbonyl groups can form *hydrogen bonds* between adjacent chains. The positive hydrogen atoms in the N-H groups of one chain are strongly attracted to the oxygen atoms in the C=O groups on another. Polymers that contain *urea* linkages would fall into this category. The structural formula for urea is shown in figure 10.6. Polymers that contain urea linkages have high tensile strength and a high melting point.



Figure 10.6: The structural formula for urea

• Dipole-dipole bonds between adjacent chains

Polyesters have *dipole-dipole bonding* between their polymer chains. Dipole bonding is not as strong as hydrogen bonding, so a polyester's melting point and strength are lower

than those of the polymers where there are hydrogen bonds between the chains. However, the weaker bonds between the chains means that polyesters have greater flexibility. The greater the flexibility of a polymer, the more likely it is to be moulded or stretched into fibres.

• Weak van der Waal's forces

Other molecules such as ethene do not have a permanent dipole and so the attractive forces between polyethene chains arise from weak *van der Waals* forces. Polyethene therefore has a lower melting point than many other polymers.

10.4 Types of polymers

There are many different types of polymers. Some are organic, while others are inorganic. Organic polymers can be broadly grouped into either synthetic/semi-synthetic (artificial) or biological (natural) polymers. We are going to take a look at two groups of organic polymers: *plastics*, which are usually synthetic or semi-synthetic and *biological macromolecules* which are natural polymers. Both of these groups of polymers play a very important role in our lives.

10.5 Plastics

In today's world, we can hardly imagine life without plastic. From cellphones to food packaging, fishing line to plumbing pipes, compact discs to electronic equipment, plastics have become a very important part of our daily lives. "Plastics" cover a range of synthetic and semi-synthetic organic polymers. Their name comes from the fact that they are 'malleable', in other words their shape can be changed and moulded.



Definition: Plastic

Plastic covers a range of synthetic or semisynthetic organic polymers. Plastics may contain other substances to improve their performance. Their name comes from the fact that many of them are malleable, in other words they have the property of plasticity.

It was only in the nineteenth century that it was discovered that plastics could be made by chemically changing natural polymers. For centuries before this, only natural organic polymers had been used. Examples of natural organic polymers include *waxes* from plants, *cellulose* (a plant polymer used in fibres and ropes) and *natural rubber* from rubber trees. But in many cases, these natural organic polymers didn't have the characteristics that were needed for them to be used in specific ways. Natural rubber for example, is sensitive to temperature and becomes sticky and smelly in hot weather and brittle in cold weather.

In 1834 two inventors, Friedrich Ludersdorf of Germany and Nathaniel Hayward of the US, independently discovered that adding sulfur to raw rubber helped to stop the material from becoming sticky. After this, Charles Goodyear discovered that heating this modified rubber made it more resistant to abrasion, more elastic and much less sensitive to temperature. What these inventors had done was to improve the properties of a natural polymer so that it could be used in new ways. An important use of rubber now is in vehicle tyres, where these properties of rubber are critically important.



The first true plastic (i.e. one that was not based on any material found in nature) was *Bakelite*, a cheap, strong and durable plastic. Some of these plastics are still used for example in electronic circuit boards, where their properties of insulation and heat resistance are very important.

10.5.1 The uses of plastics

There is such a variety of different plastics available, each having their own specific properties and uses. The following are just a few examples.

• Polystyrene

Polystyrene (figure 15.2) is a common plastic that is used in model kits, disposable eating utensils and a variety of other products. In the polystyrene polymer, the monomer is *styrene*, a liquid hydrocarbon that is manufactured from petroleum.



Figure 10.7: The polymerisation of a styrene monomer to form a polystyrene polymer

• Polyvinylchloride (PVC)

Polyvinyl chloride (PVC) (figure 10.8) is used in plumbing, gutters, electronic equipment, wires and food packaging. The side chains of PVC contain chlorine atoms, which give it its particular characteristics.



Figure 10.8: Polyvinyl chloride



Many vinyl products have other chemicals added to them to give them particular properties. Some of these chemicals, called additives, can leach out of the vinyl products. In PVC, *plasticizers* are used to make PVC more flexible. Because many baby toys are made from PVC, there is concern that some of these products may leach into the mouths of the babies that are chewing on them. In the USA, most companies have stopped making PVC toys. There are also concerns that some of the plasticizers added to PVC may cause a number of health conditions including cancer.

• Synthetic rubber

Another plastic that was critical to the World War 2 effort was *synthetic rubber*, which was produced in a variety of forms. Not only were worldwide natural rubber supplies limited,

but most rubber-producing areas were under Japanese control. Rubber was needed for tyres and parts of war machinery. After the war, synthetic rubber also played an important part in the space race and nuclear arms race.

• Polyethene/polyethylene (PE)

Polyethylene (figure 10.1) was discovered in 1933. It is a cheap, flexible and durable plastic and is used to make films and packaging materials, containers and car fittings. One of the most well known polyethylene products is 'Tupperware', the sealable food containers designed by Earl Tupper and promoted through a network of housewives!

• Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene (figure 10.9) is more commonly known as 'Teflon' and is most well known for its use in non-stick frying pans. Teflon is also used to make the breathable fabric Gore-Tex.



Figure 10.9: A tetra fluoroethylene monomer and polytetrafluoroethylene polymer

Table 10.1 summarises the formulae, properties and uses of some of the most common plastics.

Name	Formula	Monomer	Properties	Uses
Polyethene (low den-	$-(CH_2-CH_2)_n-$	$CH_2 = CH_2$	soft, waxy solid	film wrap and plastic
sity)				bags
Polyethene (high den-	$-(CH_2-CH_2)_n-$	$CH_2 = CH_2$	rigid	electrical insulation,
sity)				bottles and toys
Polypropene	$-[CH_2-CH(CH_3)]_n$ -	$CH_2 = CHCH_3$	different grades:	carpets and uphol-
			some are soft and	stery
			others hard	
Polyvinylchloride	-(CH ₂ -CHCl) _n -	CH ₂ =CHCI	strong, rigid	pipes, flooring
(PVC)				
Polystyrene	$-[CH_2-CH(C_6H_5)]_n$	$CH_2 = CHC_6H_5$	hard, rigid	toys, packaging
Polytetrafluoroethylene	$-(CF_2-CF_2)_n$ -	$CF_2 = CF_2$	resistant, smooth,	non-stick surfaces,
			solid	electrical insulation

Tab	le 10.1:	A summary	of the	formulae,	properties	and	uses o	f some	common	plastics
-----	----------	-----------	--------	-----------	------------	-----	--------	--------	--------	----------



Exercise: Plastics

 It is possible for macromolecules to be composed of more than one type of repeating monomer. The resulting polymer is called a **copolymer**. Varying the monomers that combine to form a polymer, is one way of controlling the properties of the resulting material. Refer to the table below which shows a number of different copolymers of rubber, and answer the questions that follow:

Monomer A	Monomer B	Copolymer	Uses
$H_2C = CHCI$	$H_2C = CCI_2$	Saran	films and fi-
			bres
$H_2C = CHC_6H_5$	$H_2C=C-CH=CH_2$	SBR (styrene	tyres
		butadiene	
		rubber)	
$H_2C = CHCN$	$H_2C=C-CH=CH_2$	Nitrile rubber	adhesives and
			hoses
$H_2C=C(CH_3)_2$	$H_2C=C-CH=CH_2$	Butyl rubber	inner tubes
$F_2C = CF(CF_3)$	$H_2C=CHF$	Viton	gaskets

(a) Give the structural formula for each of the monomers of nitrile rubber.

- (b) Give the structural formula of the copolymer viton.
- (c) In what ways would you expect the properties of SBR to be different from nitrile rubber?
- (d) Suggest a reason why the properties of these polymers are different.
- In your home, find as many examples of different types of plastics that you can. Bring them to school and show them to your group. Together, use your examples to complete the following table:

Object	Type of plastic	Properties	Uses

10.5.2 Thermoplastics and thermosetting plastics

A **thermoplastic** is a plastic that can be melted to a liquid when it is heated and freezes to a brittle, glassy state when it is cooled enough. These properties of thermoplastics are mostly due to the fact that the forces between chains are weak. This also means that these plastics can be easily stretched or moulded into any shape. Examples of thermoplastics include nylon, polystyrene, polyethylene, polypropylene and PVC. Thermoplastics are more easily recyclable than some other plastics.

Thermosetting plastics differ from thermoplastics because once they have been formed, they cannot be remelted or remoulded. Examples include bakelite, vulcanised rubber, melanine (used to make furniture), and many glues. Thermosetting plastics are generally stronger than thermoplastics and are better suited to being used in situations where there are high temperatures. They are not able to be recycled. Thermosetting plastics have strong covalent bonds between chains and this makes them very strong.

Activity :: Case Study : Biodegradable plastics

Read the article below and then answer the questions that follow.

Our whole world seems to be wrapped in plastic. Almost every product we buy, most of the food we eat and many of the liquids we drink come encased in plastic. Plastic packaging provides excellent protection for the product, it is cheap to manufacture and seems to last forever. Lasting forever, however, is proving to be a major environmental problem. Another problem is that traditional plastics are manufactured from non-renewable resources - oil, coal and natural gas. In an effort to overcome these problems, researchers and engineers have been trying to develop biodegradable plastics that are made from renewable resources, such as plants.

The term biodegradable means that a substance can be broken down into simpler substances by the activities of living organisms, and therefore is unlikely to remain in the environment. The reason most plastics are not biodegradable is because their long polymer molecules are too large and too tightly bonded together to be broken apart and used by decomposer organisms. However, plastics based on natural plant polymers that come from wheat or corn starch have molecules that can be more easily broken down by microbes.

Starch is a natural polymer. It is a white, granular carbohydrate produced by plants during photosynthesis and it serves as the plant's energy store. Many plants contain large amounts of starch. Starch can be processed directly into a bioplastic but, because it is soluble in water, articles made from starch will swell and deform when exposed to moisture, and this limits its use. This problem can be overcome by changing starch into a different polymer. First, starch is harvested from corn, wheat or potatoes, then microorganisms transform it into lactic acid, a monomer. Finally, the lactic acid is chemically treated to cause the molecules of lactic acid to link up into long chains or polymers, which bond together to form a plastic called polylactide (PLA).

PLA can be used for products such as plant pots and disposable nappies. It has been commercially available in some countries since 1990, and certain blends have proved successful in medical implants, sutures and drug delivery systems because they are able to dissolve away over time. However, because PLA is much more expensive than normal plastics, it has not become as popular as one would have hoped.

Questions

- 1. In your own words, explain what is meant by a 'biodegradable plastic'.
- 2. Using your knowledge of chemical bonding, explain why some polymers are biodegradable and others are not.
- 3. Explain why lactic acid is a more useful monomer than starch, when making a biodegradable plastic.
- 4. If you were a consumer (shopper), would you choose to buy a biodegradable plastic rather than another? Explain your answer.
- 5. What do you think could be done to make biodegradable plastics more popular with consumers?

10.5.3 Plastics and the environment

Although plastics have had a huge impact globally, there is also an environmental price that has to be paid for their use. The following are just some of the ways in which plastics can cause damage to the environment.

1. Waste disposal

Plastics are not easily broken down by micro-organisms and therefore most are not easily biodegradeable. This leads to waste dispoal problems.

2. Air pollution

When plastics burn, they can produce toxic gases such as carbon monoxide, hydrogen cyanide and hydrogen chloride (particularly from PVC and other plastics that contain chlorine and nitrogen).

3. Recycling

It is very difficult to recycle plastics because each type of plastic has different properties and so different recycling methods may be needed for each plastic. However, attempts are being made to find ways of recycling plastics more effectively. Some plastics can be remelted and re-used, while others can be ground up and used as a filler. However, one of the problems with recycling plastics is that they have to be sorted according to plastic *type*. This process is difficult to do with machinery, and therefore needs a lot of labour. Alternatively, plastics should be re-used. In many countries, including South Africa, shoppers must now pay for plastic bags. This encourages people to collect and re-use the bags they already have.

Activity :: Case Study : Plastic pollution in South Africa

Read the following extract, taken from 'Planet Ark' (September 2003), and then answer the questions that follow.

South Africa launches a programme this week to exterminate its "national flower" - the millions of used plastic bags that litter the landscape. Beginning on Friday, plastic shopping bags used in the country must be both thicker and more recyclable, a move officials hope will stop people from simply tossing them away. "Government has targeted plastic bags because they are the most visible kind of waste," said Phindile Makwakwa, spokeswoman for the Department of Environmental Affairs and Tourism. "But this is mostly about changing people's mindsets about the environment."

South Africa is awash in plastic pollution. Plastic bags are such a common eyesore that they are dubbed "roadside daisies" and referred to as the national flower. Bill Naude of the Plastics Federation of South Africa said the country used about eight billion plastic bags annually, a figure which could drop by 50 percent if the new law works.

It is difficult sometimes to imagine exactly how much waste is produced in our country every year. Where does all of this go to? You are going to do some simple calculations to try to estimate the volume of plastic packets that is produced in South Africa every year.

- 1. Take a plastic shopping packet and squash it into a tight ball.
 - (a) Measure the approximate length, breadth and depth of your squashed plastic bag.
 - (b) Calculate the approximate volume that is occupied by the packet.
 - (c) Now calculate the approximate volume of your classroom by measuring its length, breadth and height.
 - (d) Calculate the number of squashed plastic packets that would fit into a classroom of this volume.
 - (e) If South Africa produces an average of 8 billion plastic bags each year, how many clasrooms would be filled if all of these bags were thrown away and not re-used?
- 2. What has South Africa done to try to reduce the number of plastic bags that are produced?
- 3. Do you think this has helped the situation?
- 4. What can you do to reduce the amount of plastic that you throw away?

10.6 Biological Macromolecules

A *biological macromolecule* is one that is found in living organisms. Biological macromolecules include molecules such as carbohydrates, proteins and nucleic acids. Lipids are also biological macromolecules. They are essential for all forms of life to survive.

Definition: Biological macromolecule A biological macromolecule is a polymer that occurs naturally in living organisms. These molecules are essential to the survival of life.

10.6.1 Carbohydrates

Carbohydrates include the sugars and their polymers. One key characteristic of the carbohydrates is that they contain only the elements carbon, hydrogen and oxygen. In the carbohydrate monomers, every carbon except one has a hydroxyl group attached to it, and the remaining carbon atom is double bonded to an oxygen atom to form a carbonyl group. One of the most important monomers in the carbohydrates is **glucose** (figure 10.10). The glucose molecule can exist in an open-chain (acyclic) and ring (cyclic) form.



Figure 10.10: The open chain (a) and cyclic (b) structure of a glucose molecule

Glucose is produced during **photosynthesis**, which takes place in plants. During photosynthesis, sunlight (solar energy), water and carbon dioxide are involved in a chemical reaction that produces glucose and oxygen. This glucose is stored in various ways in the plant.

The photosynthesis reaction is as follows:

$$6CO_2 + 6H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6O_2$$

Glucose is an important source of **energy** for both the plant itself, and also for the other animals and organisms that may feed on it. Glucose plays a critical role in **cellular respiration**, which is a chemical reaction that occurs in the cells of all living organisms. During this reaction, glucose and oxygen react to produce carbon dioxide, water and ATP energy. ATP is a type of energy that can be used by the body's cells so that they can function normally. The purpose of *eating* then, is to obtain glucose which the body can then convert into the ATP energy it needs to be able to survive.

The reaction for cellular respiration is as follows:

$$6C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + ATP$$
 (cell energy)

We don't often eat glucose in its simple form. More often, we eat complex carbohydrates that our bodies have to break down into individual glucose molecules before they can be used in cellular respiration. These complex carbohydrates are polymers, which form through condensation polymerisation reactions (figure 10.11). *Starch* and *cellulose* are two example of carbohydrates that are polymers composed of glucose monomers.



Figure 10.11: Two glucose monomers (a) undergo a condensation reaction to produce a section of a carbohydrate polymer (b). One molecule of water is produced for every two monomers that react.

• Starch

Starch is used by plants to store excess glucose, and consists of long chains of glucose monomers. Potatoes are made up almost entirely of starch. This is why potatoes are such a good source of energy. Animals are also able to store glucose, but in this case it is stored as a compound called **glycogen**, rather than as starch.

• Cellulose

Cellulose is also made up of chains of glucose molecules, but the bonding between the polymers is slightly different from that in starch. Cellulose is found in the cell walls of plants and is used by plants as a building material.



It is very difficult for animals to digest the cellulose in plants that they may have been feeding on. However, fungi and some protozoa are able to break down cellulose. Many animals, including termites and cows, use these organisms to break cellulose down into glucose, which they can then use more easily.

10.6.2 Proteins

Proteins are an incredibly important part of any cell, and they carry out a number of functions such as support, storage and transport within the body. The monomers of proteins are called **amino acids**. An amino acid is an organic molecule that contains a carboxyl and an amino group, as well as a carbon side chain. The carbon side chain varies from one amino acid to the next, and is sometimes simply represented by the letter 'R' in a molecule's structural formula. Figure 10.12 shows some examples of different amino acids.



Figure 10.12: Three amino acids: glycine, alanine and serine

Although each of these amino acids has the same basic structure, their side chains ('R' groups) are different. In the amino acid glycine, the side chain consists only of a hydrogen atom, while alanine has a *methyl* side chain. The 'R' group in serine is CH_2 - OH. Amongst other things, the side chains affect whether the amino acid is *hydrophilic* (attracted to water) or *hydrophobic* (repelled by water). If the side chain is *polar*, then the amino acid is hydrophilic, but if the side chain is *non-polar* then the amino acid is hydrophobic. Glycine and alanine both have non-polar side chains, while serine has a polar side chain.



Extension: Charged regions in an amino acid

In an amino acid, the amino group acts as a base because the nitrogen atom has a pair of unpaired electrons which it can use to bond to a hydrogen ion. The amino group therefore attracts the hydrogen ion from the carboxyl group, and ends up having a charge of +1. The carboxyl group from which the hydrogen ion has been taken then has a charge of -1. The amino acid glycine can therefore also be represented as shown in the figure below.



When two amino acid monomers are close together, they may be joined to each other by **peptide bonds** (figure 10.13) to form a **polypeptide** chain. The reaction is a condensation reaction. Polypeptides can vary in length from a few amino acids to a thousand or more. The polpeptide chains are then joined to each other in different ways to form a **protein**. It is the sequence of the amino acids in the polymer that gives a protein its particular properties.

The sequence of the amino acids in the chain is known as the protein's **primary structure**. As the chain grows in size, it begins to twist, curl and fold upon itself. The different parts of the polypeptide are held together by hydrogen bonds, which form between hydrogen atoms in one part of the chain and oxygen or nitrogen atoms in another part of the chain. This is known as the **secondary structure** of the protein. Sometimes, in this coiled helical structure, bonds may form between the side chains (R groups) of the amino acids. This results in even more irregular contortions of the protein. This is called the **tertiary structure** of the protein.



Figure 10.13: Two amino acids (glycine and alanine) combine to form part of a polypeptide chain. The amino acids are joined by a peptide bond between a carbon atom of one amino acid and a nitrogen atom of the other amino acid.



There are twenty different amino acids that exist. All cells, both plant and animal, build their proteins from only twenty amino acids. At first, this seems like a very small number, especially considering the huge number of different proteins that exist. However, if you consider that most proteins are made up of polypeptide chains that contain at least 100 amino acids, you will start to realise the endless possible combinations of amino acids that are available.

The functions of proteins

Proteins have a number of functions in living organisms.

- Structural proteins such as collagen in animal connective tissue and keratin in hair, horns and feather quills, all provide support.
- Storage proteins such as albumin in egg white provide a source of energy. Plants store proteins in their seeds to provide energy for the new growing plant.
- *Transport proteins* transport other substances in the body. Haemoglobin in the blood for example, is a protein that contains iron. Haemoglobin has an affinity (attraction) for oxygen and so this is how oxygen is transported around the body in the blood.
- *Hormonal proteins* coordinate the body's activities. Insulin for example, is a hormonal protein that controls the sugar levels in the blood.
- Enzymes are chemical catalysts and speed up chemical reactions. Digestive enzymes such as salivary amylase in your saliva, help to break down polymers in food. Enzymes play an important role in all cellular reactions such as respiration, photosynthesis and many others.

Activity :: Research Project : Macromolecules in our daily diet

1. In order to keep our bodies healthy, it is important that we eat a balanced diet with the right amounts of carbohydrates, proteins and fats. Fats are an important source of energy, they provide insulation for the body, and they also provide a protective layer around many vital organs. Our bodies also need certain essential vitamins and minerals. Most food packaging has a label that provides this information.

Choose a number of different food items that you eat. Look at the food label for each, and then complete the following table:

Food	Carbohydrates (%)	Proteins (%)	Fats (%)

- (a) Which food type contains the largest proportion of protein?
- (b) Which food type contains the largest proportion of carbohydrates?
- (c) Which of the food types you have listed would you consider to be the 'healthiest'? Give a reason for your answer.
- 2. In an effort to lose weight, many people choose to *diet*. There are many diets on offer, each of which is based on particular theories about how to lose weight most effectively. Look at the list of diets below:
 - Vegetarian diet
 - Low fat diet
 - Atkin's diet

• Weight Watchers

For each of these diets, answer the following questions:

- (a) What theory of weight loss does each type of diet propose?
- (b) What are the *benefits* of the diet?
- (c) What are the potential problems with the diet?

10.6

Exercise: Carbohydrates and proteins

- 1. Give the structural formula for each of the following:
 - (a) A polymer chain, consisting of three glucose molecules.
 - (b) A polypeptide chain, consisting of two molecules of alanine and one molecule of serine.
- 2. Write balanced equations to show the polymerisation reactions that produce the polymers described above.
- 3. The following polypeptide is the end product of a polymerisation reaction:



- (a) Give the structural formula of the monomers that make up the polypeptide.
- (b) On the structural formula of the first monomer, label the amino group and the carboxyl group.
- (c) What is the chemical formula for the carbon side chain in the second monomer?
- (d) Name the bond that forms between the monomers of the polypeptide.

10.6.3 Nucleic Acids

You will remember that we mentioned earlier that each protein is different because of its unique sequence of amino acids. But what controls how the amino acids arrange themselves to form the specific proteins that are needed by an organism? This task is for the **gene**. A gene contains DNA (deoxyribonucleic acid) which is a polymer that belongs to a class of compounds called the **nucleic acids**. DNA is the genetic material that organisms inherit from their parents. It is DNA that provides the genetic coding that is needed to form the specific proteins that an organism needs. Another nucleic acid is RNA (ribonucleic acid).

The DNA polymer is made up of monomers called **nucleotides**. Each nucleotide has three parts: a sugar, a phosphate and a nitrogenous base. The diagram in figure 10.14 may help you to understand this better.


Figure 10.14: Nucleotide monomers make up the DNA polymer

There are five different nitrogenous bases: adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U). It is the sequence of the nitrogenous bases in a DNA polymer that will determine the genetic code for that organism. Three consecutive nitrogenous bases provide the coding for one amino acid. So, for example, if the nitrogenous bases on three nucleotides are *uracil*, *cytosine* and *uracil* (in that order), one **serine** amino acid will become part of the polypeptide chain. The polypeptide chain is built up in this way until it is long enough (and with the right amino acid sequence) to be a protein. Since proteins control much of what happens in living organisms, it is easy to see how important nucleic acids are as the starting point of this process.



A single defect in even one nucleotide, can be devastating to an organism. One example of this is a disease called **sickle cell anaemia**. Because of one wrong nucletide in the genetic code, the body produces a protein called **sickle haemoglobin**. Haemoglobin is the protein in red blood cells that helps to transport oxygen around the body. When sickle haemoglobin is produced, the red blood cells change shape. This process damages the red blood cell membrane, and can cause the cells to become stuck in blood vessels. This then means that the red blood cells, which are carrying oxygen, can't get to the tissues where they are needed. This can cause serious organ damage. Individuals who have sickle cell anaemia generally have a lower life expectancy.

Table 10.2 shows some other examples of genetic coding for different amino acids.



Nitrogenous base se	equence Amino acid
UUU	Phenylalanine
CUU	Leucine
UCU	Serine
UAU	Tyrosine
UGU	Cysteine
GUU	Valine
GCU	Alanine
GGU	Glycine

Table 10.2: Nitrogenouse base sequences and the corresponding amino acid

- 1. For each of the following, say whether the statement is **true** or **false**. If the statement is *false*, give a reason for your answer.
 - (a) Deoxyribonucleic acid (DNA) is an example of a *polymer* and a nucleotide is an example of a *monomer*.
 - (b) Thymine and uracil are examples of nucleotides.
 - (c) A person's DNA will determine what proteins their body will produce, and therefore what characteristics they will have.
 - (d) An amino acid is a protein monomer.
 - (e) A polypeptide that consists of five amino acids, will also contain five nucleotides.
- 2. For each of the following sequences of nitrogenous bases, write down the amino acid/s that will be part of the polypeptide chain.
 - (a) UUU
 - (b) UCUUUU
 - (c) GGUUAUGUUGGU
- 3. A polypeptide chain consists of three amino acids. The sequence of nitrogenous bases in the nucleotides of the DNA is GCUGGUGCU. Give the structural formula of the polypeptide.

10.7 Summary

- A **polymer** is a macromolecule that is made up of many repeating structural units called **monomers** which are joined by covalent bonds.
- Polymers that contain carbon atoms in the main chain are called organic polymers.
- Organic polymers can be divided into **natural organic polymers** (e.g. natural rubber) or **synthetic organic polymers** (e.g. polystyrene).
- The polymer **polyethene** for example, is made up of many ethene monomers that have been joined into a polymer chain.
- Polymers form through a process called **polymerisation**.
- Two examples of polymerisation reactions are addition and condensation reactions.
- An addition reaction occurs when unsaturated monomers (e.g. alkenes) are added to each other one by one. The breaking of a double bond between carbon atoms in the monomer, means that a bond can form with the next monomer. The polymer **polyethene** is formed through an addition reaction.

- In a **condensation reaction**, a molecule of water is released as a product of the reaction. The water molecule is made up of atoms that have been lost from each of the monomers. Polyesters and nylon are polymers that are produced through a condensation reaction.
- The **chemical properties** of polymers (e.g. tensile strength and melting point) are determined by the types of atoms in the polymer, and by the strength of the bonds between adjacent polymer chains. The stronger the bonds, the greater the strength of the polymer, and the higher its melting point.
- One group of synthetic organic polymers, are the plastics.
- **Polystyrene** is a plastic that is made up of styrene monomers. Polystyrene is used a lot in packaging.
- **Polyvinyl chloride** (PVC) consists of vinyl chloride monomers. PVC is used to make pipes and flooring.
- **Polyethene**, or **polyethylene**, is made from ethene monomers. Polyethene is used to make film wrapping, plastic bags, electrical insulation and bottles.
- Polytetrafluoroethylene is used in non-stick frying pans and electrical insulation.
- A **thermoplastic** can be heated and melted to a liquid. It freezes to a brittle, glassy state when cooled very quickly. Examples of thermoplastics are polyethene and PVC.
- A **thermoset** plastic cannot be melted or re-shaped once formed. Examples of thermoset plastics are vulcanised rubber and melanine.
- It is not easy to recycle all plastics, and so they create environmental problems.
- Some of these **environmental problems** include issues of waste disposal, air pollution and recycling.
- A biological macromolecule is a polymer that occurs naturally in living organisms.
- Examples of biological macromolecules include **carbohydrates** and **proteins**, both of which are essential for life to survive.
- Carbohydrates include the sugars and their polymers, and are an important source of energy in living organisms.
- Glucose is a carbohydrate monomer. Glucose is the molecule that is needed for photosynthesis in plants.
- The glucose monomer is also a building block for carbohydrate polymers such as **starch**, **glycogen** and **cellulose**.
- **Proteins** have a number of important functions. These include their roles in structures, transport, storage, hormonal proteins and enzymes.
- A protein consists of monomers called amino acids, which are joined by peptide bonds.
- A protein has a primary, secondary and tertiary structure.
- An amino acid is an organic molecule, made up of a **carboxyl** and an **amino** group, as well as a carbon **side chain** of varying lengths.
- It is the sequence of amino acids that determines the nature of the protein.
- It is the **DNA** of an organism that determines the order in which amino acids combine to make a protein.
- DNA is a nucleic acid. DNA is a polymer, and is made up of monomers called nucleotides.
- Each nucleotide consists of a **sugar**, a **phosphate** and a **nitrogenous base**. It is the sequence of the nitrogenous bases that provides the 'code' for the arrangement of the amino acids in a protein.

205

Exercise: Summary exercise

- 1. Give one word for each of the following descriptions:
 - (a) A chain of monomers joined by covalent bonds.
 - (b) A polymerisation reaction that produces a molecule of water for every two monomers that bond.
 - (c) The bond that forms between an alcohol and a carboxylic acid monomer during a polymerisation reaction.
 - (d) The name given to a protein monomer.
 - (e) A six-carbon sugar monomer.
 - (f) The monomer of DNA, which determines the sequence of amino acids that will make up a protein.
- For each of the following questions, choose the one correct answer from the list provided.
 - (a) A polymer is made up of monomers, each of which has the formula $CH_2=CHCN$. The formula of the polymer is:
 - i. -($CH_2 = CHCN$)_n-
 - ii. $-(CH_2-CHCN)_n$ -
 - iii. $-(CH-CHCN)_n$ -
 - iv. -(CH_3 -CHCN)_n-
 - (b) A polymer has the formula $-[CO(CH_2)_4CO-NH(CH_2)6NH]_n$. Which of the following statements is **true**?
 - i. The polymer is the product of an addition reaction.
 - ii. The polymer is a polyester.
 - iii. The polymer contains an amide linkage.
 - iv. The polymer contains an ester linkage.
 - (c) Glucose...
 - i. is a monomer that is produced during cellular respiration
 - ii. is a sugar polymer
 - iii. is the monomer of starch
 - iv. is a polymer produced during photosynthesis
- 3. The following monomers are involved in a polymerisation reaction:



- (a) Give the structural formula of the polymer that is produced.
- (b) Is the reaction an addition or condensation reaction?
- (c) To what group of organic compounds do the two monomers belong?
- (d) What is the name of the monomers?
- (e) What type of bond forms between the monomers in the final polymer?
- 4. The table below shows the melting point for three plastics. Suggest a reason why the melting point of PVC is *higher* than the melting point for polyethene, but *lower* than that for polyester.

Plastic	Melting point (⁰ C)
Polyethene	105 - 115
PVC	212
Polyester	260

- 5. An amino acid has the formula $H_2NCH(CH_2CH_2SCH_3)COOH$.
 - (a) Give the structural formula of this amino acid.
 - (b) What is the chemical formula of the carbon side chain in this molecule?
 - (c) Are there any peptide bonds in this molecule? Give a reason for your answer.

Part III Chemical Change

Chapter 11

Physical and Chemical Change -Grade 10

Matter is all around us. The desks we sit at, the air we breathe and the water we drink, are all examples of matter. But matter doesn't always stay the same. It can change in many different ways. In this chapter, we are going to take a closer look at **physical** and **chemical** changes that occur in matter.

11.1 Physical changes in matter

A **physical change** is one where the particles of the substances that are involved in the change are not broken up in any way. When water is heated for example, the temperature and energy of the water molecules increases and the liquid water evaporates to form water vapour. When this happens, some kind of change has taken place, but the molecular structure of the water has not changed. This is an example of a *physical change*.

 $H_2O(l) \to H_2O(g)$

Conduction (the transfer of energy through a material) is another example of a physical change. As energy is transferred from one material to another, the *energy* of each material is changed, but not its chemical makeup. Dissolving one substance in another is also a physical change.



Definition: Physical change

A change that can be seen or felt, but that doesn't involve the break up of the particles in the reaction. During a physical change, the *form* of matter may change, but not its *identity*. A change in temperature is an example of a physical change.

There are some important things to remember about physical changes in matter:

• Arrangement of particles

When a physical change occurs, the particles (e.g. atoms, molecules) may re-arrange themselves without actually breaking up in any way. In the example of evaporation that we used earlier, the water molecules move further apart as their temperature (and therefore energy) increases. The same would be true if ice were to melt. In the solid phase, water molecules are packed close together in a very ordered way, but when the ice is heated, the molecules overcome the forces holding them together and they move apart. Once again, the particles have re-arranged themselves, but have not broken up.

$$\begin{array}{c} H_2O(s) \to H_2O(l) \\ \\ 211 \end{array}$$



Figure 11.1: The arrangement of water molecules in the three phases of matter

Figure 11.1 shows this more clearly. In each phase of water, the water molecule itself stays the same, but the way the molecules are arranged has changed.

In a physical change, the total mass, the number of atoms and the number of molecules will always stay the same.

Energy changes

Energy changes may take place when there is a physical change in matter, but these energy changes are normally smaller than the energy changes that take place during a chemical change.

• Reversibility

Physical changes in matter are usually easier to reverse than chemical changes. Water vapour for example, can be changed back to liquid water if the temperature is lowered. Liquid water can be changed into ice by simply increasing the temperature, and so on.

11.2 Chemical Changes in Matter

When a **chemical change** takes place, new substances are formed in a chemical reaction. These new products may have very different properties from the substances that were there at the start of the reaction.

The breakdown of copper(II) chloride to form copper and chlorine is an example of chemical change. A simplified diagram of this reaction is shown in figure 11.2. In this reaction, the initial substance is copper(II) chloride but, once the reaction is complete, the products are copper and chlorine.



 $CuCl_2 \rightarrow Cu + Cl_2$





Definition: Chemical change

The formation of new substances in a chemical reaction. One type of matter is changed into something different.

There are some important things to remember about chemical changes:

• Arrangement of particles

During a chemical change, the particles themselves are changed in some way. In the example of copper (II) chloride that was used earlier, the CuCl₂ molecules were split up into their component atoms. The number of particles will change because each one CuCl₂ molecule breaks down into one copper atom (Cu) and one chlorine molecule (Cl₂). However, what you should have noticed, is that the number of atoms of each element stays the same, as does the total mass of the atoms. This will be discussed in more detail in a later section.

• Energy changes

The energy changes that take place during a chemical reaction are much greater than those that take place during a physical change in matter. During a chemical reaction, energy is used up in order to break bonds, and then energy is released when the new product is formed. This will be discussed in more detail in section **??**.

• Reversibility

Chemical changes are far more difficult to reverse than physical changes.

Two types of chemical reactions are decomposition reactions and synthesis reactions.

11.2.1 Decomposition reactions

A **decomposition reaction** occurs when a chemical compound is broken down into elements or smaller compounds. The generalised equation for a decomposition reaction is:

$$AB \rightarrow A + B$$

One example of such a reaction is the decomposition of hydrogen peroxide (figure 11.3) to form hydrogen and oxygen according to the following equation:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$



Figure 11.3: The decomposition of H_2O_2 to form H_2O and O_2

The decomposition of mercury (II) oxide is another example.

Activity :: Experiment : The decomposition of mercury (II) oxide Aim:

To observe the decomposition of mercury (II) oxide when it is heated.

Note: Because this experiment involves mercury, which is a poisonous substance, it should be done in a fume cupboard, and all the products of the reaction must be very carefully disposed of.

Apparatus:

Mercury (II) oxide (an orange-red product); two test tubes; a large beaker; stopper and delivery tube; Bunsen burner; wooden splinter.



Method:

- 1. Put a small amount of mercury (II) oxide in a test tube and heat it gently over a Bunsen burner. Then allow it to cool. What do you notice about the colour of the mercury (II) oxide?
- 2. Heat the test tube again, and note what happens. Do you notice anything on the walls of the test tube? Record these observations.
- 3. Test for the presence of oxygen using a glowing splinter.

Results:

- During the first heating of mercury (II) oxide, the only change that took place was a change in colour from orange-red to black and then back to its original colour.
- When the test tube was heated again, deposits of mercury formed on the inner surface of the test tube. What colour is this mercury?
- The glowing splinter burst into flame when it was placed in the test tube, meaning that oxygen is present.

Conclusions:

When mercury is heated, it decomposes to form mercury and oxygen. The chemical decomposition reaction that takes place can be written as follows:

$$2HgO \rightarrow 2Hg + O_2$$

11.2.2 Synthesis reactions

During a **synthesis reaction**, a new product is formed from smaller elements or compounds. The generalised equation for a synthesis reaction is as follows:

$$\begin{array}{c} A+B \to AB\\ 214 \end{array}$$

One example of a synthesis reaction is the burning of magnesium in oxygen to form magnesium oxide. The equation for the reaction is:

$$2Mg + O_2 \rightarrow 2MgO$$

Figure 11.4 shows the chemical changes that take place at a microscopic level during this chemical reaction.



Figure 11.4: The synthesis of magnesium oxide (MgO) from magnesium and oxygen

Activity :: Experiment : Chemical reactions involving iron and sulfur Aim:

To demonstrate the synthesis of iron sulfide from iron and sulfur. **Apparatus:**

5.6 g iron filings and 3.2 g powdered sulfur; porcelain dish; test tube; bunsen burner



Method:

- 1. Before you carry out the experiment, write a balanced equation for the reaction you expect will take place.
- 2. Measure the quantity of iron and sulfur that you need and mix them in a porcelain dish.
- 3. Take some of this mixture and place it in the test tube. The test tube should be about 1/3 full.
- 4. This reaction should ideally take place in a fume cupboard. Heat the test tube containing the mixture over the Bunsen burner. Increase the heat if no reaction takes place. Once the reaction begins, you will need to remove the test tube from the flame. Record your observations.

- 5. Wait for the product to cool before breaking the test tube with a hammer. Make sure that the test tube is rolled in paper before you do this, otherwise the glass will shatter everywhere and you may be hurt.
- 6. What does the product look like? Does it look anything like the original reactants? Does it have any of the properties of the reactants (e.g. the magnetism of iron)?

Results:

- After you removed the test tube from the flame, the mixture glowed a bright red colour. The reaction is exothermic and *produces energy*.
- The product, iron sulfide, is a dark colour and does not share any of the properties of the original reactants. It is an entirely new product.

Conclusions:

A synthesis reaction has taken place. The equation for the reaction is:

 $Fe+S \to FeS$

Activity :: Investigation : Physical or chemical change? Apparatus:

Bunsen burner, 4 test tubes, a test tube rack and a test tube holder, small spatula, pipette, magnet, a birthday candle, NaCl (table salt), 0.1M AgNO₃, 6M HCl, magnesium ribbon, iron filings, sulfur.

Method:

- 1. Place a small amount of wax from a birthday candle into a test tube and heat it over the bunsen burner until it melts. Leave it to cool.
- 2. Add a small spatula of NaCl to 5 ml water in a test tube and shake. Then use the pipette to add 10 drops of $AgNO_3$ to the sodium chloride solution.
- 3. Take a 5 cm piece of magnesium ribbon and tear it into 1 cm pieces. Place two of these pieces into a test tube and add a few drops of 6M HCI. NOTE: Be very careful when you handle this acid because it can cause major burns.
- 4. Take about 0.5 g iron filings and 0.5 g sulfur. Test each substance with a magnet. Mix the two samples in a test tube, and run a magnet alongside the outside of the test tube.
- 5. Now heat the test tube that contains the iron and sulfur. What changes do you see? What happens now, if you run a magnet along the outside of the test tube?
- 6. In each of the above cases, record your observations.

Questions:

Decide whether each of the following changes are physical or chemical and give a reason for your answer in each case. Record your answers in the table below:

Description	Physical chemical change	or	Reason
melting candle wax			
dissolving NaCl			
mixing NaCl with AgNO ₃			
tearing magnesium ribbon			
adding HCI to magnesium ribbon			
mixing iron and sulfur			
heating iron and sulfur			

11.3 Energy changes in chemical reactions

All reactions involve some change in energy. During a *physical* change in matter, such as the evaporation of liquid water to water vapour, the energy of the water molecules increases. However, the change in energy is much smaller than in chemical reactions.

When a chemical reaction occurs, some bonds will *break*, while new bonds may *form*. Energy changes in chemical reactions result from the breaking and forming of bonds. For bonds to *break*, energy must be *absorbed*. When new bonds *form*, energy will be *released* because the new product has a lower energy than the 'inbetween' stage of the reaction when the bonds in the reactants have just been broken.

In some reactions, the energy that must be *absorbed* to break the bonds in the reactants, is less than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy is *released*. This type of reaction is known as an **exothermic** reaction. In other reactions, the energy that must be *absorbed* to break the bonds in the reactants, is more than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy must be *absorbed* from the surroundings. This type of reaction is known as an **endothermic** reaction. In the earlier part of this chapter, most decomposition reactions were endothermic, and heating was needed for the reaction to occur. Most of the synthesis reactions were exothermic, meaning that energy was given off in the form of heat or light.

More simply, we can describe the energy changes that take place during a chemical reaction as:

Total energy absorbed to break bonds - Total energy released when new bonds form

So, for example, in the reaction...

$$2Mg + O_2 \rightarrow 2MgO$$

Energy is needed to break the O-O bonds in the oxygen molecule so that new Mg-O bonds can be formed, and energy is released when the product (MgO) forms.

Despite all the energy changes that seem to take place during reactions, it is important to remember that energy cannot be created or destroyed. Energy that enters a system will have come from the surrounding environment, and energy that leaves a system will again become part of that environment. This principle is known as the principle of **conservation of energy**.



Definition: Conservation of energy principle Energy cannot be created or destroyed. It can only be changed from one form to another.

Chemical reactions may produce some very visible, and often violent, changes. An explosion, for example, is a sudden increase in volume and release of energy when high temperatures are generated and gases are released. For example, NH_4NO_3 can be heated to generate nitrous oxide. Under these conditions, it is highly sensitive and can detonate easily in an explosive exothermic reaction.

11.4 Conservation of atoms and mass in reactions

The total mass of all the substances taking part in a chemical reaction is conserved during a chemical reaction. This is known as the **law of conservation of mass**. The total number of **atoms** of each element also remains the same during a reaction, although these may be arranged differently in the products.

We will use two of our earlier examples of chemical reactions to demonstrate this:

• The decomposition of hydrogen peroxide into water and oxygen

$$2H_2O_2 \to 2H_2O + O_2$$



Left hand side of the equation Total atomic mass = $(4 \times 1) + (4 \times 16) = 68$ u Number of atoms of each element = $(4 \times H) + (4 \times O)$

Right hand side of the equation

Total atomic mass = $(4 \times 1) + (2 \times 16) + (2 \times 16) = 68$ u Number of atoms of each element = $(4 \times H) + (4 \times O)$

Both the atomic mass and the number of atoms of each element are conserved in the reaction.

• The synthesis of magnesium and oxygen to form magnesium oxide

$$2Mg + O_2 \rightarrow 2MgO$$



Left hand side of the equation

Total atomic mass = $(2 \times 24.3) + (2 \times 16) = 80.6$ u

Number of atoms of each element = (2 \times Mg) + (2 \times O)

Right hand side of the equation

Total atomic mass = $(2 \times 24.3) + (2 \times 16) = 80.6$ u Number of atoms of each element = $(2 \times Mg) + (2 \times O)$

Both the atomic mass and the number of atoms of each element are conserved in the reaction.

Activity :: Demonstration : The conservation of atoms in chemical reactions

Materials:

[•] Coloured marbles or small balls to represent atoms. Each colour will represent a different element.

• Prestik

Method:

1. Choose a reaction from any that have been used in this chapter or any other *balanced* chemical reaction that you can think of. To help to explain this activity, we will use the decomposition reaction of calcium carbonate to produce carbon dioxide and calcium oxide.

$$CaCO_3 \rightarrow CO_2 + CaO$$

- Stick marbles together to represent the reactants and put these on one side of your table. In this example you may for example join one red marble (calcium), one green marble (carbon) and three yellow marbles (oxygen) together to form the molecule calcium carbonate (CaCO₃).
- 3. Leaving your reactants on the table, use marbles to make the product molecules and place these on the other side of the table.
- 4. Now count the number of atoms on each side of the table. What do you notice?
- 5. Observe whether there is any difference between the molecules in the reactants and the molecules in the products.

Discussion

You should have noticed that the number of atoms in the reactants is the same as the number of atoms in the product. The number of atoms is conserved during the reaction. However, you will also see that the molecules in the reactants and products is not the same. The *arrangement of atoms* is not conserved during the reaction.

11.5 Law of constant composition

In any given chemical compound, the elements always combine in the same proportion with each other. This is the **law of constant proportions**.

The **law of constant composition** says that, in any particular chemical compound, all samples of that compound will be made up of the same elements in the same proportion or ratio. For example, any water molecule is always made up of two hydrogen atoms and one oxygen atom in a 2:1 ratio. If we look at the relative masses of oxygen and hydrogen in a water molecule, we see that 94% of the mass of a water molecule is accounted for by oxygen, and the remaining 6% is the mass of hydrogen. This mass proportion will be the same for any water molecule.

This does not mean that hydrogen and oxygen always combine in a 2:1 ratio to form H_2O . Multiple proportions are possible. For example, hydrogen and oxygen may combine in different proportions to form H_2O_2 rather than H_2O . In H_2O_2 , the H:O ratio is 1:1 and the mass ratio of hydrogen to oxygen is 1:16. This will be the same for any molecule of hydrogen peroxide.

11.6 Volume relationships in gases

In a chemical reaction between gases, the relative volumes of the gases in the reaction are present in a ratio of small whole numbers if all the gases are at the same temperature and pressure. This relationship is also known as **Gay-Lussac's Law**.

For example, in the reaction between hydrogen and oxygen to produce water, two volumes of H_2 react with 1 volume of O_2 to produce 2 volumes of H_2O .

$$2H_2 + O_2 \rightarrow 2H_2O$$

In the reaction to produce ammonia, one volume of nitrogen gas reacts with three volumes of hydrogen gas to produce two volumes of ammonia gas.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

This relationship will also be true for all other chemical reactions.

11.7 Summary

- Matter does not stay the same. It may undergo physical or chemical changes
- A **physical change** means that the form of matter may change, but not its identity. For example, when water evaporates, the energy and the arrangement of water molecules will change, but not the structure of the water molecule itself.
- During a physical change, the **arrangement of particles** may change but the mass, number of atoms and number of molecules will stay the same.
- Physical changes involve small changes in energy, and are easily reversible.
- A chemical change occurs when one form of matter changes into something else. A chemical reaction involves the formation of new substances with **different properties**. For example, carbon dioxide reacts with water to form carbonic acid.

$$CO_2 + H_2O \rightarrow H_2CO_3$$

- A chemical change may involve a **decomposition** or **synthesis** reaction. During chemical change, the mass and number of atoms is conserved, but the number of molecules is not always the same.
- Chemical reactions involve larger changes in energy. During a reaction, energy is needed to break bonds in the reactants, and energy is released when new products form. If the energy released is greater than the energy absorbed, then the reaction is exothermic. If the energy released is less than the energy absorbed, then the reaction is endothermic. These chemical reactions are not easily reversible.
- Decomposition reactions are usually **endothermic** and synthesis reactions are usually **exothermic**.
- The **law of conservation of mass** states that the total mass of all the substances taking part in a chemical reaction is conserved and the number of atoms of each element in the reaction does not change when a new product is formed.
- The **conservation of energy principle** states that energy cannot be created or destroyed, it can only change from one form to another.
- The **law of constant composition** states that in any particular compound, all samples of that compound will be made up of the same elements in the same proportion or ratio.
- Gay-Lussac's Law states that in a chemical reaction between gases, the relative volumes of the gases in the reaction are present in a ratio of small whole numbers if all the gases are at the same temperature and pressure.



Exercise: Summary exercise

1. Complete the following table by saying whether each of the descriptions is an example of a physical or chemical change:

Description	Physical chemical	or
hot and cold water mix together		
milk turns sour		
a car starts to rust		
food digests in the stomach		
alcohol disappears when it is placed on your skin		
warming food in a microwave		
separating sand and gravel		
fireworks exploding		

- 2. For each of the following reactions, say whether it is an example of a synthesis or decomposition reaction:
 - (a) $(NH_4)_2CO_3 \rightarrow 2NH_3 + CO_2 + H_2O$
 - (b) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
 - (c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3$
 - (d) $CaCO_3(s) \rightarrow CaO + CO_2$
- 3. For the following equation:

$$CaCO_3 \rightarrow CO_2 + CaO$$

Show that the 'law of conservation of mass' applies.

Chapter 12

Representing Chemical Change -Grade 10

As we have already mentioned, a number of changes can occur when elements react with one another. These changes may either be *physical* or *chemical*. One way of representing these changes is through **balanced chemical equations**. A chemical equation describes a chemical reaction by using symbols for the elements involved. For example, if we look at the reaction between iron (Fe) and sulfur (S) to form iron sulfide (FeS), we could represent these changes either in words or using chemical symbols:

iron + sulfur \rightarrow iron sulfide or $Fe + S \rightarrow FeS$

Another example would be:

ammonia + oxygen \rightarrow nitric oxide + water or $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

Compounds on the left of the arrow are called the **reactants** and these are needed for the reaction to take place. In this equation, the reactants are ammonia and oxygen. The compounds on the right are called the **products** and these are what is formed from the reaction.

In order to be able to write a balanced chemical equation, there are a number of important things that need to be done:

- 1. Know the chemical symbols for the elements involved in the reaction
- 2. Be able to write the chemical formulae for different reactants and products
- 3. Balance chemical equations by understanding the laws that govern chemical change
- 4. Know the state symbols for the equation

We will look at each of these steps separately in the next sections.

12.1 Chemical symbols

It is very important to know the chemical symbols for common elements in the Periodic Table so that you are able to write chemical equations and to recognise different compounds.

12.2

Exercise: Revising common chemical symbols

- Write down the chemical symbols and names of all the elements that you know.
- Compare your list with another learner and add any symbols and names that you don't have.
- Spend some time, either in class or at home, learning the symbols for at least the first twenty elements in the periodic table. You should also learn the symbols for other common elements that are not in the first twenty.
- Write a short test for someone else in the class and then exchange tests with them so that you each have the chance to answer one.

12.2 Writing chemical formulae

A **chemical formula** is a concise way of giving information about the atoms that make up a particular chemical compound. A chemical formula shows each element by its symbol, and also shows how many atoms of each element are found in that compound. The number of atoms (if greater than one) is shown as a subscript.

Examples:

CH₄ (methane)

Number of atoms: $(1 \times \text{carbon}) + (4 \times \text{hydrogen}) = 5$ atoms in one methane molecule

H_2SO_4 (sulfuric acid)

Number of atoms: $(2 \times hydrogen) + (1 \times sulfur) + (4 \times oxygen) = 7$ atoms in one molecule of sulfuric acid

A chemical formula may also give information about how the atoms are arranged in a molecule if it is written in a particular way. A molecule of ethane, for example, has the chemical formula C_2H_6 . This formula tells us how many atoms of each element are in the molecule, but doesn't tell us anything about how these atoms are arranged. In fact, each carbon atom in the ethane molecule is bonded to three hydrogen atoms. Another way of writing the formula for ethane is CH_3CH_3 . The number of atoms of each element has not changed, but this formula gives us more information about how the atoms are arranged in relation to each other.

The slightly tricky part of writing chemical formulae comes when you have to work out the ratio in which the elements combine. For example, you may know that sodium (Na) and chlorine (Cl) react to form sodium chloride, but how do you know that in each molecule of sodium chloride there is only *one* atom of sodium for every *one* atom of chlorine? It all comes down to the **valency** of an atom or group of atoms. Valency is the number of bonds that an element can form with another element. Working out the chemical formulae of chemical compounds using their valency, will be covered in chapter 4. For now, we will use formulae that you already know.

12.3 Balancing chemical equations

12.3.1 The law of conservation of mass

In order to balance a chemical equation, it is important to understand the law of conservation of mass.

Definition: The law of conservation of mass

The mass of a closed system of substances will remain constant, regardless of the processes acting inside the system. Matter can change form, but cannot be created or destroyed. For any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

In a chemical equation then, the **mass** of the reactants must be equal to the mass of the products. In order to make sure that this is the case, the number of **atoms** of each element in the reactants must be equal to the number of atoms of those same elements in the products. Some examples are shown below:

Example 1:

$$Fe + S \rightarrow FeS$$



Reactants

Atomic mass of reactants = 55.8 u + 32.1 u = 87.9 u

Number of atoms of each element in the reactants: $(1 \times Fe)$ and $(1 \times S)$

Products

Atomic mass of product = 55.8 u + 32.1 u = 87.9 u

Number of atoms of each element in the products: $(1 \times Fe)$ and $(1 \times S)$

Since the number of atoms of each element is the same in the reactants and in the products, we say that the equation is **balanced**.

Example 2:

$$H_2 + O_2 \rightarrow H_2O$$



Reactants

Atomic mass of reactants = (1 + 1) + (16 + 16) = 34 uNumber of atoms of each element in the reactants: $(2 \times H)$ and $(2 \times O)$

Product

Atomic mass of product = (1 + 1 + 16) = 18 u

Number of atoms of each element in the products: $(2 \times H)$ and $(1 \times O)$

Since the total atomic mass of the reactants and the products is not the same, and since there are more oxygen atoms in the reactants than there are in the product, the equation is **not balanced**.

Example 3:

 $NaOH + HCl \rightarrow NaCl + H_2O$



Reactants

Atomic mass of reactants = (23 + 16 + 1) + (1 + 35.4) = 76.4 u Number of atoms of each element in the reactants: $(1 \times Na) + (1 \times O) + (2 \times H) + (1 \times CI)$

Products

Atomic mass of products = (23 + 35.4) + (1 + 1 + 16) = 76.4 u Number of atoms of each element in the products: $(1 \times Na) + (1 \times O) + (2 \times H) + (1 \times CI)$ Since the number of atoms of each element is the same in the reactants and in the products, we say that the equation is **balanced**.

We now need to find a way to balance those equations that are not balanced so that the number of atoms of each element in the reactants is the same as that for the products. This can be done by changing the **coefficients** of the molecules until the atoms on each side of the arrow are balanced. You will see later in chapter 13 that these coefficients tell us something about the **mole ratio** in which substances react. They also tell us about the volume relationship between gases in the reactants and products.

Important: Coefficients

Remember that if you put a number in front of a molecule, that number applies to the *whole* molecule. For example, if you write $2H_2O$, this means that there are 2 molecules of water. In other words, there are 4 hydrogen atoms and 2 oxygen atoms. If we write 3HCl, this means that there are 3 molecules of HCl. In other words there are 3 hydrogen atoms and 3 chlorine atoms in total. In the first example, 2 is the coefficient and in the second example, 3 is the coefficient.

12.3.2 Steps to balance a chemical equation

When balancing a chemical equation, there are a number of steps that need to be followed.

- STEP 1: Identify the reactants and the products in the reaction, and write their chemical formulae.
- STEP 2: Write the equation by putting the reactants on the left of the arrow, and the products on the right.
- STEP 3: Count the number of atoms of each element in the reactants and the number of atoms of each element in the products.
- STEP 4: If the equation is not balanced, change the coefficients of the molecules until the number of atoms of each element on either side of the equation balance.
- STEP 5: Check that the atoms are in fact balanced.
- STEP 6 (we will look at this a little later): Add any extra details to the equation e.g. phase.



Worked Example 49: Balancing chemical equations 1

Question: Balance the following equation:

 $Mg + HCl \rightarrow MgCl_2 + H_2$

Answer

Step 1 : Because the equation has been written for you, you can move straight on to counting the number of atoms of each element in the reactants and products

Reactants: Mg = 1 atom; H = 1 atom and CI = 1 atom Products: Mg = 1 atom; H = 2 atoms and CI = 2 atoms

Step 2 : Balance the equation

The equation is not balanced since there are 2 chlorine atoms in the product and only 1 in the reactants. If we add a coefficient of 2 to the HCl to increase the number of H and Cl atoms in the reactants, the equation will look like this:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Step 3 : Check that the atoms are balanced

If we count the atoms on each side of the equation, we find the following: Reactants: Mg = 1; H = 2; CI = 2Products: Mg = 1; H = 2; CI = 2The equation is balanced. The final equation is:

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$



Worked Example 50: Balancing chemical equations 2

Question: Balance the following equation:

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

Answer

Step 1 : Count the number of atoms of each element in the reactants and products Reactants: C = 1; H = 4; O = 2

Products: C = 1; H = 2; O = 3

Step 2 : Balance the equation

If we add a coefficient of 2 to H_2O , then the number of hydrogen atoms in the reactants will be 4, which is the same as for the reactants. The equation will be:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

Step 3 : Check that the atoms balance

Reactants: C = 1; H = 4; O = 2Products: C = 1; H = 4; O = 4

You will see that, although the number of *hydrogen* atoms now balances, there are more oxygen atoms in the products. You now need to repeat the previous step. If we put a coefficient of 2 in front of O_2 , then we will increase the number of oxygen atoms in the reactants by 2. The new equation is:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

When we check the number of atoms again, we find that the number of atoms of each element in the reactants is the same as the number in the products. The equation is now balanced.

Worked Example 51: Balancing chemical equations 3

Question: Nitrogen gas reacts with hydrogen gas to form ammonia. Write a balanced chemical equation for this reaction.

Answer

Step 1 : Identify the reactants and the products, and write their chemical formulae

The reactants are nitrogen (N_2) and hydrogen (H_2) , and the product is ammonia (NH_3) .

Step 2 : Write the equation so that the reactants are on the left and products on the right of the arrow

The equation is as follows:

$$N_2 + H_2 \rightarrow NH_3$$

Step 3 : Count the atoms of each element in the reactants and products Reactants: N = 2; H = 2 Products: N = 1; H = 3

Step 4 : Balance the equation

In order to balance the number of nitrogen atoms, we could rewrite the equation as:

$$N_2 + H_2 \rightarrow 2NH_3$$

Step 5 : Check that the atoms are balanced

In the above equation, the nitrogen atoms now balance, but the hydrogen atoms don't (there are 2 hydrogen atoms in the reactants and 6 in the product). If we put a coefficient of 3 in front of the hydrogen (H_2), then the hydrogen atoms and the nitrogen atoms balance. The final equation is:

$$N_2 + 3H_2 \rightarrow 2NH_3$$



Worked Example 52: Balancing chemical equations 4

Question: In our bodies, sugar $(\rm C_6H_{12}O_6)$ reacts with the oxygen we breathe in to produce carbon dioxide, water and energy. Write the balanced equation for this reaction.

Answer

Step 1 : Identify the reactants and products in the reaction, and write their chemical formulae.

Reactants: sugar $(C_6H_{12}O_6)$ and oxygen (O_2) Products: carbon dioxide (CO_2) and water (H_2O)

Step 2 : Write the equation by putting the reactants on the left of the arrow, and the products on the right

$$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$$

Step 3 : Count the number of atoms of each element in the reactants and the number of atoms of each element in the products

Reactants: C=6; H=12; O=8; Products: C=1; H=2; O=3;

Step 4 : Change the coefficients of the molecules until the number of atoms of each element on either side of the equation balance.

It is easier to start with carbon as it only appears once on each side. If we add a 6 in front of CO_2 , the equation looks like this:

$$C_6 H_{12} O_6 + O_2 \to 6 C O_2 + H_2 O_3$$

Reactants: C=6; H=12; O=8; Products: C=6; H=2; O=13;

Step 5 : Change the coefficients again to try to balance the equation. Let's try to get the number of hydrogens the same this time.

$$C_6H_{12}O_6 + O_2 \to 6CO_2 + 6H_2O$$

Reactants: C=6; H=12; O=8; Products: C=6; H=12; O=18;

Step 6 : Now we just need to balance the oxygen atoms.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O_2$$

Reactants: C=6; H=12; O=18; Products: C=6; H=12; O=18;

?

Exercise: Balancing simple chemical equations

Balance the following equations:

1. Hydrogen fuel cells are extremely important in the development of alternative energy sources. Many of these cells work by reacting hydrogen and oxygen gases together to form water, a reaction which also produces electricity. Balance the following equation:

$$H_2(g) + O_2(g) \rightarrow H_2O(l)$$

2. The synthesis of ammonia (NH_3) , made famous by the German chemist Fritz Haber in the early 20th century, is one of the most important reactions in the chemical industry. Balance the following equation used to produce ammonia:

$$N_2(g) + H_2(g) \rightarrow NH_3(g)$$

- 3. $Mg + P_4 \rightarrow Mg_3P_2$
- 4. $Ca + H_2O \rightarrow Ca(OH)_2 + H_2$
- 5. $CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2$
- 6. $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + NaCl$
- 7. $C_{12}H_{22}O_{11} + O_2 \rightarrow CO_2 + H_2O$
- 8. Barium chloride reacts with sulphuric acid to produce barium sulphate and hydrochloric acid.
- 9. Ethane (C_2H_6) reacts with oxygen to form carbon dioxide and steam.
- 10. Ammonium carbonate is often used as a smelling salt. Balance the following reaction for the decomposition of ammonium carbonate:

$$(NH_4)_2CO_3(s) \to NH_3(aq) + CO_2(g) + H_2O(l)$$

12.4 State symbols and other information

The state (phase) of the compounds can be expressed in the chemical equation. This is done by placing the correct label on the right hand side of the formula. There are only four labels that can be used:

- 1. (g) for gaseous compounds
- 2. (I) for liquids
- 3. (s) for solid compounds
- 4. (aq) for an aqueous (water) solution

Occasionally, a catalyst is added to the reaction. A catalyst is a substance that speeds up the reaction without undergoing any change to itself. In a chemical equation, this is shown by using the symbol of the catalyst above the arrow in the equation.

To show that heat was needed for the reaction, a Greek delta (Δ) is placed above the arrow in the same way as the catalyst.

Important: You may remember from chapter 11 that energy cannot be created or destroyed during a chemical reaction but it may change form. In an exothermic reaction, ΔH is less than zero, and in an endothermic reaction, ΔH is greater than zero. This value is often written at the end of a chemical equation.



Worked Example 53: Balancing chemical equations 4

Question: Solid zinc metal reacts with aqueous hydrochloric acid to form an aqueous solution of zinc chloride ($ZnCl_2$)and hydrogen gas. Write a balanced equation for this reaction.

Answer

Step 1 : Identify the reactants and products and their chemical formulae The reactants are zinc (Zn) and hydrochloric acid (HCl). The products are zinc chloride (ZnCl₂) and hydrogen (H₂).

Step 2 : Place the reactants on the left of the equation and the products on the right hand side of the arrow.

$$Zn + HCl \rightarrow ZnCl_2 + H_2$$

Step 3 : Balance the equation

You will notice that the zinc atoms balance but the chlorine and hydrogen atoms don't. Since there are two chlorine atoms on the right and only one on the left, we will give HCl a coefficient of 2 so that there will be two chlorine atoms on each side of the equation.

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Step 4 : Check that all the atoms balance

When you look at the equation again, you will see that all the atoms are now balanced.

Step 5 : Ensure all details (e.g. state symbols) are added

In the initial description, you were told that zinc was a metal, hydrochloric acid and zinc chloride were in aqueous solutions and hydrogen was a gas.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Worked Example 54: Balancing chemical equations 5 (advanced)

Question: Balance the following equation:

 $(NH_4)_2SO_4 + NaOH \rightarrow NH_3 + H_2O + Na_2SO_4$

In this example, the first two steps are not necessary because the reactants and products have already been given.

Answer

Step 1 : Balance the equation

With a complex equation, it is always best to start with atoms that appear only once on each side i.e. Na, N and S atoms. Since the S atoms already balance, we will start with Na and N atoms. There are two Na atoms on the right and one on the left. We will add a second Na atom by giving NaOH a coefficient of two. There are two N atoms on the left and one on the right. To balance the N atoms, NH_3 will be given a coefficient of two. The equation now looks as follows:

 $(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + H_2O + Na_2SO_4$

Step 2 : Check that all atoms balance

N, Na and S atoms balance, but O and H atoms do not. There are six O atoms and ten H atoms on the left, and five O atoms and eight H atoms on the right. We need to add one O atom and two H atoms on the right to balance the equation. This is done by adding another H_2O molecule on the right hand side. We now need to check the equation again:

 $(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + 2H_2O + Na_2SO_4$

The equation is now balanced.



Exercise: Balancing more advanced chemical equations Write balanced equations for each of the following reactions:

- 1. $Al_2O_3(s) + H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$
- 2. $Mg(OH)_2(aq) + HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + 2H_2O(l)$
- 3. Lead(II)nitrate solution reacts with potassium iodide solution.
- When heated, aluminium reacts with solid copper oxide to produce copper metal and aluminium oxide (Al₂O₃).
- 5. When calcium chloride solution is mixed with silver nitrate solution, a white precipitate (solid) of silver chloride appears. Calcium nitrate $(Ca(NO_3)_2)$ is also produced in the solution.

12.5 Summary

- A chemical equation uses symbols to describe a chemical reaction.
- In a chemical equation, **reactants** are written on the left hand side of the equation, and the **products** on the right. The arrow is used to show the direction of the reaction.
- When representing chemical change, it is important to be able to write the **chemical** formula of a compound.
- In any chemical reaction, the **law of conservation of mass** applies. This means that the total atomic mass of the reactants must be the same as the total atomic mass of the products. This also means that the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the product.
- If the number of atoms of each element in the reactants is the same as the number of atoms of each element in the product, then the equation is **balanced**.
- If the number of atoms of each element in the reactants is not the same as the number of atoms of each element in the product, then the equation is **not balanced**.
- In order to balance an equation, **coefficients** can be placed in front of the reactants and products until the number of atoms of each element is the same on both sides of the equation.

?

Exercise: Summary exercise

Balance each of the following chemical equations:

- 1. $NH_4 + H_2O \rightarrow NH_4OH$
- Sodium chloride and water react to form sodium hydroxide, chlorine and hydrogen.
- Propane is a fuel that is commonly used as a heat source for engines and homes. Balance the following equation for the combustion of propane:

$$C_3H_8(l) + O_2(g) \to CO_2(g) + H_2O(l)$$

- 4. Aspartame, an artificial sweetener, has the formula $C_{14}H_{18}N_2O_5$. Write the balanced equation for its combustion (reaction with O_2) to form CO_2 gas, liquid H_2O , and N_2 gas.
- 5. $Fe_2(SO_4)_3 + K(SCN) \rightarrow K_3Fe(SCN)_6 + K_2SO_4$
- 6. Chemical weapons were banned by the Geneva Protocol in 1925. According to this protocol, all chemicals that release suffocating and poisonous gases are not to be used as weapons. White phosphorus, a very reactive allotrope of phosphorus, was recently used during a military attack. Phosphorus burns vigorously in oxygen. Many people got severe burns and some died as a result. The equation for this spontaneous reaction is:

$$P_4(s) + O_2(g) \to P_2O_5(s)$$

- (a) Balance the chemical equation.
- (b) Prove that the law of conservation of mass is obeyed during this chemical reaction.
- (c) Name the product formed during this reaction.
- (d) Classify the reaction as endothermic or exothermic. Give a reason for your answer.
- (e) Classify the reaction as a sythesis or decomposition reaction. Give a reason for your answer.

(DoE Exemplar Paper 2 2007)

12.5

Chapter 13

Quantitative Aspects of Chemical Change - Grade 11

An equation for a chemical reaction can provide us with a lot of useful information. It tells us what the reactants and the products are in the reaction, and it also tells us the ratio in which the reactants combine to form products. Look at the equation below:

$$Fe + S \rightarrow FeS$$

In this reaction, every atom of iron (Fe) will react with a single atom of sulfur (S) to form one molecule of iron sulfide (FeS). However, what the equation doesn't tell us, is the **quantities** or the **amount** of each substance that is involved. You may for example be given a small sample of iron for the reaction. How will you know how many atoms of iron are in this sample? And how many atoms of sulfur will you need for the reaction to use up all the iron you have? Is there a way of knowing what mass of iron sulfide will be produced at the end of the reaction? These are all very important questions, especially when the reaction is an industrial one, where it is important to know the quantities of reactants that are needed, and the quantity of product that will be formed. This chapter will look at how to quantify the changes that take place in chemical reactions.

13.1 The Mole

Sometimes it is important to know exactly how many particles (e.g. atoms or molecules) are in a sample of a substance, or what quantity of a substance is needed for a chemical reaction to take place.

You will remember from chapter 3 that the **relative atomic mass** of an element, describes the mass of an atom of that element relative to the mass of an atom of carbon-12. So the mass of an atom of carbon (relative atomic mass is 12 u) for example, is twelve times greater than the mass of an atom of hydrogen, which has a relative atomic mass of 1 u. How can this information be used to help us to know what mass of each element will be needed if we want to end up with the same number of *atoms* of carbon and hydrogen?

Let's say for example, that we have a sample of 12g carbon. What mass of *hydrogen* will contain the same number of atoms as 12 g carbon? We know that each atom of carbon weighs twelve times more than an atom of hydrogen. Surely then, we will only need 1g of hydrogen for the number of atoms in the two samples to be the same? You will notice that the number of particles (in this case, *atoms*) in the two substances is the same when the ratio of their sample masses (12g carbon: 1g hydrogen = 12:1) is the same as the ratio of their relative atomic masses (12 u: 1 u = 12:1).

To take this a step further, if you were to weigh out samples of a number of elements so that the mass of the sample was the same as the relative atomic mass of that element, you would find that the number of particles in each sample is 6.023×10^{23} . These results are shown in table 13.1 below for a number of different elements. So, 24.31 g of magnesium (relative atomic mass = 24.31 u) for example, has the same number of atoms as 40.08 g of calcium (relative atomic mass = 40.08 u).

Table 13.1: Table s	showing the relations	hip between	the sample mass,	the relative	atomic mass
and the number of	atoms in a sample, f	or a number	of elements.		

Element	Relative atomic mass (u)	Sample mass (g)	Atoms in sample
Hydrogen (H)	1.01	1.01	6.023 x 10 ²³
Carbon (C)	12.01	12.01	6.023 x 10 ²³
Magnesium (Mg)	24.31	24.31	6.023 x 10 ²³
Sulfur (S)	32.07	32.07	6.023 x 10 ²³
Calcium (Ca)	40.08	40.08	6.023 x 10 ²³

This result is so important that scientists decided to use a special unit of measurement to define this quantity: the **mole** or 'mol'. A **mole** is defined as being an amount of a substance which contains the same number of particles as there are atoms in 12 g of carbon. In the examples that were used earlier, 24.31 g magnesium is *one mole* of magnesium, while 40.08 g of calcium is *one mole* of calcium. A mole of any substance always contains the same number of particles.



Definition: Mole

The mole (abbreviation 'n') is the SI (Standard International) unit for 'amount of substance'. It is defined as an amount of substance that contains the same number of particles (atoms, molecules or other particle units) as there are atoms in 12 g carbon.

In one mole of any substance, there are 6.023 x 10^{23} particles. This is known as **Avogadro's** number.



Definition: Avogadro constant

The number of particles in a mole, equal to 6.023×10^{23} . It is also sometimes referred to as the number of atoms in 12 g of carbon-12.



The original hypothesis that was proposed by Amadeo Avogadro was that 'equal volumes of gases, at the same temperature and pressure, contain the same number of molecules'. His ideas were not accepted by the scientific community and it was only four years after his death, that his original hypothesis was accepted and that it became known as 'Avogadro's Law'. In honour of his contribution to science, the number of particles in one mole was named Avogadro's number.



Exercise: Moles and mass

1. Complete the following table:

Element	Relative atomic mass (u)	Sample mass (g)	Number of moles in the sample
Hydrogen	1.01	1.01	
Magnesium	24.31	24.31	
Carbon	12.01	24.02	
Chlorine	35.45	70.9	
Nitrogen		42.08	

- 2. How many atoms are there in...
 - (a) 1 mole of a substance
 - (b) 2 moles of calcium
 - (c) 5 moles of phosphorus
 - (d) 24.31 g of magnesium
 - (e) 24.02 g of carbon

13.2 Molar Mass

Definition: Molar mass

Molar mass (M) is the mass of 1 mole of a chemical substance. The unit for molar mass is grams per mole or $g.mol^{-1}$.

Refer to table 13.1. You will remember that when the mass, in grams, of an element is equal to its relative atomic mass, the sample contains one mole of that element. This mass is called the **molar mass** of that element.

It is worth remembering the following: On the Periodic Table, the relative atomic mass that is shown can be interpreted in two ways.

- 1. The mass of a *single, average atom* of that element relative to the mass of an atom of carbon.
- 2. The mass of one mole of the element. This second use is the molar mass of the element.

Table 13.2: The relationship between relative atomic mass, molar mass and the mass of one mole for a number of elements.

Element	Relative atomic mass (u)	Molar mass $(g.mol^{-1})$	Mass of one mole of the element (g)
Magnesium	24.31	24.31	24.31
Lithium	6.94	6.94	6.94
Oxygen	16	16	16
Nitrogen	14.01	14.01	14.01
Iron	55.85	55.85	55.85



Worked Example 55: Calculating the number of moles from mass

Question: Calculate the number of moles of iron (Fe) in a 111.7 g sample.

Answer

Step 1 : Find the molar mass of iron

If we look at the periodic table, we see that the molar mass of iron is 55.85 g.mol^{-1} . This means that 1 mole of iron will have a mass of 55.85 g.mol^{-1} .

Step 2 : Use the molar mass and sample mass to calculate the number of moles of iron

If 1 mole of iron has a mass of 55.85 g, then: the number of moles of iron in 111.7 g must be:

$$\frac{111.7g}{55.85g.mol^{-1}} = 2mol$$

There are 2 moles of iron in the sample.



Worked Example 56: Calculating mass from moles

Question: You have a sample that contains 5 moles of zinc.

1. What is the mass of the zinc in the sample?

2. How many atoms of zinc are in the sample?

Answer

Step 1 : Find the molar mass of zinc

Molar mass of zinc is 65.38 g.mol^{-1} , meaning that 1 mole of zinc has a mass of 65.38 g.

Step 2 : Calculate the mass of zinc, using moles and molar mass.

If 1 mole of zinc has a mass of 65.38 g, then 5 moles of zinc has a mass of:

 $65.38 \text{ g} \times 5 \text{ mol} = 326.9 \text{ g} (\text{answer to a})$

Step 3 : Use the number of moles of zinc and Avogadro's number to calculate the number of zinc atoms in the sample.

 $5\times 6.023\times 10^{23} = 30.115\times 10^{23}$



Exercise: Moles and molar mass

- 1. Give the molar mass of each of the following elements:
 - (a) hydrogen
 - (b) nitrogen
 - (c) bromine
- 2. Calculate the number of moles in each of the following samples:
 - (a) 21.62 g of boron (B)

- (b) 54.94 g of manganese (Mn)
- (c) 100.3 g of mercury (Hg)
- (d) 50 g of barium (Ba)
- (e) 40 g of lead (Pb)

13.3 An equation to calculate moles and mass in chemical reactions

The calculations that have been used so far, can be made much simpler by using the following equation:

 $\textbf{n} \text{ (number of moles)} = \frac{\textbf{m} \text{ (mass of substance in g)}}{\textbf{M} \text{ (molar mass of substance in g} \cdot \mathrm{mol}^{-1})}$

Important: Remember that when you use the equation n = m/M, the mass is always in grams (g) and molar mass is in grams per mol (g.mol⁻¹).

The equation can also be used to calculate mass and molar mass, using the following equations:

$$m = n \times M$$

and

$$M = \frac{m}{n}$$

The following diagram may help to remember the relationship between these three variables. You need to imagine that the horizontal line is like a 'division' sign and that the vertical line is like a 'multiplication' sign. So, for example, if you want to calculate 'M', then the remaining two letters in the triangle are 'm' and 'n' and 'm' is above 'n' with a division sign between them. In your calculation then, 'm' will be the numerator and 'n' will be the denominator.





Worked Example 57: Calculating moles from mass

Question: Calculate the number of moles of copper there are in a sample that weighs 127 g.

Answer

Step 1 : Write the equation to calculate the number of moles

$$n = \frac{m}{M}$$

Step 2 : Substitute numbers into the equation

$$n = \frac{127}{63.55} = 2$$

There are 2 moles of copper in the sample.



Worked Example 58: Calculating mass from moles

Question: You are given a 5 mol sample of sodium. What mass of sodium is in the sample?

Answer Step 1 : Write the equation to calculate the sample mass.

 $m = n \times M$

Step 2 : Substitute values into the equation. $M_{Na} = 22.99 \text{ g.mol}^{-1}$

Therefore,

$$n = 5 \times 22.99 = 114.95g$$

The sample of sodium has a mass of 114.95 g.



Worked Example 59: Calculating atoms from mass

Question: Calculate the number of atoms there are in a sample of aluminium that weighs 80.94 g.

Answer

Step 1 : Calculate the number of moles of aluminium in the sample.

$$n = \frac{m}{M} = \frac{80.94}{26.98} = 3moles$$

Step 2 : Use Avogadro's number to calculate the number of atoms in the sample.

Number of atoms in 3 mol aluminium = 3 \times 6.023 \times 10^{23} There are 18.069 \times 10^{23} aluminium atoms in a sample of 80.94 g.
13.4

?

Exercise: Some simple calculations

- 1. Calculate the number of moles in each of the following samples:
 - (a) 5.6 g of calcium
 - (b) 0.02 g of manganese
 - (c) 40 g of aluminium
- 2. A lead sinker has a mass of 5 g.
 - (a) Calculate the number of moles of lead the sinker contains.
 - (b) How many lead atoms are in the sinker?
- 3. Calculate the mass of each of the following samples:
 - (a) 2.5 mol magnesium
 - (b) 12 g lithium
 - (c) 4.5 imes 10 25 atoms of silica

13.4 Molecules and compounds

So far, we have only discussed moles, mass and molar mass in relation to *elements*. But what happens if we are dealing with a molecule or some other chemical compound? Do the same concepts and rules apply? The answer is 'yes'. However, you need to remember that all your calculations will apply to the *whole molecule*. So, when you calculate the molar mass of a molecule, you will need to add the molar mass of each atom in that compound. Also, the number of moles will also apply to the whole molecule. For example, if you have one mole of nitric acid (HNO₃), it means you have 6.023×10^{23} **molecules** of nitric acid in the sample. This also means that there are 6.023×10^{23} **atoms** of hydrogen, 6.023×10^{23} **atoms** of nitrogen and ($3 \times 6.023 \times 10^{23}$) **atoms** of oxygen in the sample.

In a balanced chemical equation, the number that is written in front of the element or compound, shows the **mole ratio** in which the reactants combine to form a product. If there are no numbers in front of the element symbol, this means the number is '1'.

e.g.
$$N_2 + 3H_2 \rightarrow 2NH_3$$

In this reaction, 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia.



Worked Example 60: Calculating molar mass

Question: Calculate the molar mass of H_2SO_4 .

Answer Step 1 : Use the periodic table to find the molar mass for each element in the molecule. Hydrogen = 1.008 g.mol^{-1} ; Sulfur = 32.07 g.mol^{-1} ; Oxygen = 16 g.mol^{-1}

Step 2 : Add the molar masses of each atom in the molecule

$$M_{(H_2SO_4)} = (2 \times 1.008) + (32.07) + (4 \times 16) = 98.09g.mol^{-1}$$

×	
	Ø

Worked Example 61: Calculating moles from mass

Question: Calculate the number of moles there are in 1kg of MgCl₂.

Answer

Step 1: Write the equation for calculating the number of moles in the sample.

$$n = \frac{m}{M}$$

1. Convert mass into grams

$$m = 1kg \times 1000 = 1000g$$

2. Calculate the molar mass of $MgCl_2$.

$$M_{(MgCl_2)} = 24.31 + (2 \times 35.45) = 95.21g.mol^{-1}$$

Step 3 : Substitute values into the equation

$$n = \frac{1000}{95.21} = 10.5 mol$$

There are 10.5 moles of magnesium chloride in a 1 kg sample.



Worked Example 62: Calculating the mass of reactants and products

Question: Barium chloride and sulfuric acid react according to the following equation to produce barium sulphate and hydrochloric acid.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

If you have 2 g of $BaCl_2...$

- 1. What quantity (in g) of H_2SO_4 will you need for the reaction so that all the barium chloride is used up?
- 2. What mass of HCl is produced during the reaction?

Answer

Step 1 : Calculate the number of moles of $BaCl_2$ that react.

$$n = \frac{m}{M} = \frac{2}{208.24} = 0.0096 mol$$

Step 2 : Determine how many moles of H_2SO_4 are needed for the reaction According to the balanced equation, 1 mole of $BaCl_2$ will react with 1 mole of H_2SO_4 . Therefore, if 0.0096 moles of $BaCl_2$ react, then there must be the same number of moles of H_2SO_4 that react because their mole ratio is 1:1.

Step 3 : Calculate the mass of H_2SO_4 that is needed.

 $m = n \times M = 0.0096 \times 98.086 = 0.94g$

(answer to 1)

Step 4 : Determine the number of moles of HCl produced.

According to the balanced equation, 2 moles of HCl are produced for every 1 mole of the two reactants. Therefore the number of moles of HCl produced is (2 \times 0.0096), which equals 0.0192 moles.

Step 5 : Calculate the mass of HCI.

$$m = n \times M = 0.0192 \times 35.73 = 0.69g$$

(answer to 2)

Activity :: Group work : Understanding moles, molecules and Avogadro's number

Divide into groups of three and spend about 20 minutes answering the following questions together:

- 1. What are the units of the mole? Hint: Check the definition of the mole.
- 2. You have a 56 g sample of iron sulfide (FeS)
 - (a) How many moles of FeS are there in the sample?
 - (b) How many molecules of FeS are there in the sample?
 - (c) What is the difference between a mole and a molecule?

3. The exact size of Avogadro's number is sometimes difficult to imagine.

- (a) Write down Avogadro's number without using scientific notation.
- (b) How long would it take to count to Avogadro's number? You can assume that you can count two numbers in each second.

Exercise: More advanced calculations

- 1. Calculate the molar mass of the following chemical compounds:
 - (a) KOH
 - (b) FeCl₃
 - (c) $Mg(OH)_2$
- 2. How many moles are present in:
 - (a) 10 g of Na_2SO_4
 - (b) 34 g of $Ca(OH)_2$
 - (c) 2.45×10^{23} molecules of CH₄?

- 3. For a sample of 0.2 moles of potassium bromide (KBr), calculate...
 - (a) the number of moles of K^+ ions
 - (b) the number of moles of Br^- ions
- 4. You have a sample containing 3 moles of calcium chloride.
 - (a) What is the chemical formula of calcium chloride?
 - (b) How many calcium atoms are in the sample?
- 5. Calculate the mass of:
 - (a) 3 moles of NH_4OH
 - (b) 4.2 moles of $Ca(NO_3)_2$
- 6. 96.2 g sulfur reacts with an unknown quantity of zinc according to the following equation:

$$Zn + S \rightarrow ZnS$$

- (a) What mass of zinc will you need for the reaction, if all the sulfur is to be used up?
- (b) What mass of zinc sulfide will this reaction produce?
- 7. Calcium chloride reacts with carbonic acid to produce calcium carbonate and hydrochloric acid according to the following equation:

 $CaCl_2 + H_2CO_3 \rightarrow CaCO_3 + 2HCl$

If you want to produce 10 g of calcium carbonate through this chemical reaction, what quantity (in g) of calcium chloride will you need at the start of the reaction?

13.5 The Composition of Substances

The **empirical formula** of a chemical compound is a simple expression of the relative number of each type of atom in it. In contrast, the **molecular formula** of a chemical compound gives the actual number of atoms of each element found in a molecule of that compound.



Definition: Empirical formula

The empirical formula of a chemical compound gives the relative number of each type of atom in it.



Definition: Molecular formula

The molecular formula of a chemical compound gives the exact number of atoms of each element in one molecule of that compound.

The compound *ethanoic acid* for example, has the molecular formula CH_3COOH or simply $C_2H_4O_2$. In one molecule of this acid, there are two carbon atoms, four hydrogen atoms and two oxygen atoms. The ratio of atoms in the compound is 2:4:2, which can be simplified to 1:2:1. Therefore, the empirical formula for this compound is CH_2O . The empirical formula contains the smallest whole number ratio of the elements that make up a compound.

Knowing either the empirical or molecular formula of a compound, can help to determine its composition in more detail. The opposite is also true. Knowing the *composition* of a substance can help you to determine its formula. There are three different types of composition problems that you might come across:

- 1. Problems where you will be given the formula of the substance and asked to calculate the percentage by mass of each element in the substance.
- 2. Problems where you will be given the percentage composition and asked to calculate the formula.
- Problems where you will be given the products of a chemical reaction and asked to calculate the formula of one of the reactants. These are usually referred to as combustion analysis problems.



Worked Example 63: Calculating the percentage by mass of elements in a

compound

Question: Calculate the percentage that each element contributes to the overall mass of sulfuric acid (H_2SO_4) .

Answer

Step 1 : Write down the relative atomic mass of each element in the compound.

 $\begin{array}{l} \mbox{Hydrogen} = 1.008 \times 2 = 2.016 \mbox{ u} \\ \mbox{Sulfur} = 32.07 \mbox{ u} \\ \mbox{Oxygen} = 4 \times 16 = 64 \mbox{ u} \end{array}$

Step 2 : Calculate the molecular mass of sulfuric acid.

Use the calculations in the previous step to calculate the molecular mass of sulfuric acid.

Mass = 2.016 + 32.07 + 64 = 98.09u

$\label{eq:step 3} \mbox{Step 3}: \mbox{Convert the mass of each element to a percentage of the total mass of the compound}$

Use the equation:

Percentage by mass = atomic mass / molecular mass of $H_2SO_4 \times 100\%$

Hydrogen

$$\frac{2.016}{98.09} \times 100\% = 2.06\%$$

Sulfur

 $\frac{32.07}{98.09} \times 100\% = 32.69\%$

Oxygen

$$\frac{64}{98.09} \times 100\% = 65.25\%$$

(You should check at the end that these percentages add up to 100%!) In other words, in one molecule of sulfuric acid, hydrogen makes up 2.06% of the mass of the compound, sulfur makes up 32.69% and oxygen makes up 65.25%.



Worked Example 64: Determining the empirical formula of a compound

Question: A compound contains 52.2% carbon (C), 13.0% hydrogen (H) and 34.8% oxygen (O). Determine its empirical formula.

Answer

Step 1 : If we assume that we have 100 g of this substance, then we can convert each element percentage into a mass in grams. Carbon = 52.2 g, hydrogen = 13 g and oxygen = 34.8 g

Step 2 : Convert the mass of each element into number of moles

$$n = \frac{m}{M}$$

Therefore,

$$n(carbon) = \frac{52.2}{12.01} = 4.35mol$$
$$n(hydrogen) = \frac{13}{1.008} = 12.90mol$$
$$n(oxygen) = \frac{34.8}{16} = 2.18mol$$

Step 3 : Convert these numbers to the simplest mole ratio by dividing by the smallest number of moles

In this case, the smallest number of moles is 2.18. Therefore... *Carbon*

$$\frac{4.35}{2.18} = 2$$

Hydrogen

$$\frac{12.90}{2.18} = 6$$

Oxygen

$$\frac{2.18}{2.18} = 1$$

Therefore the empirical formula of this substance is: C_2H_6O . Do you recognise this compound?



Worked Example 65: Determining the formula of a compound

Question: 207 g of lead combines with oxygen to form 239 g of a lead oxide. Use this information to work out the formula of the lead oxide (Relative atomic masses: Pb = 207 u and O = 16 u).

Answer Step 1 : Calculate the mass of oxygen in the reactants

$$239 - 207 = 32g$$

Step 2 : Calculate the number of moles of lead and oxygen in the reactants.

 $n = \frac{m}{M}$

Lead

$$\frac{207}{207} = 1 \mod$$

Oxygen

$$\frac{32}{16}=2mol$$

Step 3 : Deduce the formula of the compound

The mole ratio of Pb:O in the product is 1:2, which means that for every atom of lead, there will be two atoms of oxygen. The formula of the compound is PbO_2 .



Worked Example 66: Empirical and molecular formula

Question: Vinegar, which is used in our homes, is a dilute form of acetic acid. A sample of acetic acid has the following percentage composition: 39.9% carbon, 6.7% hyrogen and 53.4% oxygen.

- 1. Determine the empirical formula of acetic acid.
- 2. Determine the molecular formula of acetic acid if the molar mass of acetic acid is 60g/mol.

Answer

Step 1 : Calculate the mass of each element in 100 g of acetic acid. In 100g of acetic acid, there is 39.9 g C, 6.7 g H and 53.4 g O

Step 2 : Calculate the number of moles of each element in 100 g of acetic acid.

 $n = \frac{m}{M}$

$$n_C = \frac{39.9}{12} = 3.33 \text{ mol}$$

$$n_H = \frac{6.7}{1} = 6.7 \text{ mol}$$

$$n_O = \frac{53.4}{16} = 3.34 \text{ mol}$$

Step 3 : Divide the number of moles of each element by the lowest number to get the simplest mole ratio of the elements (i.e. the empirical formula) in acetic acid.

Empirical formula is CH_2O

Step 4 : Calculate the molecular formula, using the molar mass of acetic acid.

The molar mass of acetic acid using the empirical formula is 30 g/mol. Therefore the actual number of moles of each element must be double what it is in the emprical formula.

The molecular formula is therefore $C_2H_4O_2$ or CH_3COOH

Exercise: Moles and empirical formulae

- 1. Calcium chloride is produced as the product of a chemical reaction.
 - (a) What is the formula of calcium chloride?
 - (b) What percentage does each of the elements contribute to the mass of a molecule of calcium chloride?
 - (c) If the sample contains 5 g of calcium chloride, what is the mass of calcium in the sample?
 - (d) How many moles of calcium chloride are in the sample?
- 13g of zinc combines with 6.4g of sulfur.What is the empirical formula of zinc sulfide?
 - (a) What mass of zinc sulfide will be produced?
 - (b) What percentage does each of the elements in zinc sulfide contribute to its mass?
 - (c) Determine the formula of zinc sulfide.
- 3. A calcium mineral consisted of 29.4% calcium, 23.5% sulphur and 47.1% oxygen by mass. Calculate the empirical formula of the mineral.
- A chlorinated hydrocarbon compound when analysed, consisted of 24.24% carbon, 4.04% hydrogen, 71.72% chlorine. The molecular mass was found to be 99 from another experiment. Deduce the empirical and molecular formula.

13.6 Molar Volumes of Gases

It is possible to calculate the volume of a mole of gas at STP using what we now know about gases.

1. Write down the ideal gas equation

$$pV = nRT$$
, therefore $V = \frac{nRT}{n}$

2. Record the values that you know, making sure that they are in SI units

You know that the gas is under STP conditions. These are as follows:

$$p = 101.3 \text{ kPa} = 101300 \text{ Pa}$$

$$n = 1$$
 mole

$$R = 8.3 J.K^{-1}.mol^{-1}$$

- T = 273 K
- 3. Substitute these values into the original equation.

$$V = \frac{nRT}{n}$$

$$V = \frac{1mol \times 8.3J.K^{-1}.mol^{-1} \times 273K}{101300Pa}$$

4. Calculate the volume of 1 mole of gas under these conditions

The volume of 1 mole of gas at STP is 22.4 \times 10 $^{-3}$ m 3 = 22.4 dm $^3.$

Ì

Important: The standard units used for this equation are P in Pa, V in m³ and T in K. Remember also that $1000 \text{ cm}^3 = 1 \text{ dm}^3$ and $1000 \text{ dm}^3 = 1 \text{ m}^3$.

Worked Example 67: Ideal Gas

Question: A sample of gas occupies a volume of 20 dm³, has a temperature of 280 K and has a pressure of 105 Pa. Calculate the number of moles of gas that are present in the sample.

Answer

Step 1 : Convert all values into SI units

The only value that is not in SI units is volume. $V = 0.02 \text{ m}^3$.

Step 2 : Write the equation for calculating the number of moles in a gas. We know that $pV=n\mathsf{R}\mathsf{T}$

Therefore,

$$n = \frac{pV}{RT}$$

Step 3 : Substitute values into the equation to calculate the number of moles of the gas.

$$n = \frac{105 \times 0.02}{8.31 \times 280} = \frac{2.1}{2326.8} = 0.0009$$
moles



Exercise: Using the combined gas law

- 1. An enclosed gas has a volume of 300 cm^3 and a temperature of 300 K. The pressure of the gas is 50 kPa. Calculate the number of moles of gas that are present in the container.
- 2. What pressure will 3 mol gaseous nitrogen exert if it is pumped into a container that has a volume of 25 dm³ at a temperature of 29 ⁰C?
- 3. The volume of air inside a tyre is 19 litres and the temperature is 290 K. You check the pressure of your tyres and find that the pressure is 190 kPa. How many moles of air are present in the tyre?
- 4. Compressed carbon dioxide is contained within a gas cylinder at a pressure of 700 kPa. The temperature of the gas in the cylinder is 310 K and the number of moles of gas is 13 moles carbon dioxide. What is the volume of the gas inside?

13.7 Molar concentrations in liquids

A typical solution is made by dissolving some solid substance in a liquid. The amount of substance that is dissolved in a given volume of liquid is known as the **concentration** of the liquid. Mathematically, concentration (C) is defined as moles of solute (n) per unit volume (V) of solution.

 $C = \frac{n}{V}$

For this equation, the units for volume are dm³. Therefore, the unit of concentration is mol.dm⁻³. When concentration is expressed in $mol.dm^{-3}$ it is known as the **molarity** (M) of the solution. Molarity is the most common expression for concentration.



Definition: Concentration

Concentration is a measure of the amount of solute that is dissolved in a given volume of liquid. It is measured in mol.dm⁻³. Another term that is used for concentration is **molarity (M)**



Worked Example 68: Concentration Calculations 1

Question: If 3.5 g of sodium hydroxide (NaOH) is dissolved in 2.5 dm^3 of water, what is the concentration of the solution in mol.dm⁻³?

Answer

Step 1 : Convert the mass of NaOH into moles

$$n = \frac{m}{M} = \frac{3.5}{40} = 0.0875 mol$$

Step 2 : Calculate the concentration of the solution.

$$C = \frac{n}{V} = \frac{0.0875}{2.5} = 0.035$$

The concentration of the solution is 0.035 mol.dm $^{-3}$ or 0.035 M



Worked Example 69: Concentration Calculations 2

Question: You have a 1 dm³ container in which to prepare a solution of potassium permanganate (KMnO₄). What mass of KMnO₄ is needed to make a solution with a concentration of 0.2 M?

Answer Step 1 : Calculate the number of moles of $KMnO_4$ needed.

$$C = \frac{n}{V}$$

therefore

$$n = C \times V = 0.2 \times 1 = 0.2mol$$

Step 2 : Convert the number of moles of $KMnO_4$ to mass.

 $m = n \times M = 0.2 \times 158.04 = 31.61g$

The mass of $KMnO_4$ that is needed is 31.61 g.

Worked Example 70: Concentration Calculations 3

Question: How much sodium chloride (in g) will one need to prepare 500 $\rm cm^3$ of solution with a concentration of 0.01 M?

Answer

Step 1 : Convert all quantities into the correct units for this equation.

$$V = \frac{500}{1000} = 0.5 dm^3$$

Step 2 : Calculate the number of moles of sodium chloride needed.

 $n=C\times V=0.01\times 0.5=0.005mol$

Step 3 : Convert moles of $KMnO_4$ to mass.

 $m = n \times M = 0.005 \times 58.45 = 0.29g$

The mass of sodium chloride needed is 0.29 g

Exercise: Molarity and the concentration of solutions

- 1. 5.95g of potassium bromide was dissolved in 400cm3 of water. Calculate its molarity.
- 2. 100 g of sodium chloride (NaCl) is dissolved in 450 cm^3 of water.
 - (a) How many moles of NaCl are present in solution?
 - (b) What is the volume of water (in dm³)?
 - (c) Calculate the concentration of the solution.
 - (d) What mass of sodium chloride would need to be added for the concentration to become 5.7 mol.dm⁻³?
- 3. What is the molarity of the solution formed by dissolving 80 g of sodium hydroxide (NaOH) in 500 cm³ of water?
- 4. What mass (g) of hydrogen chloride (HCl) is needed to make up 1000 cm³ of a solution of concentration 1 mol.dm⁻³?
- 5. How many moles of H_2SO_4 are there in 250 cm³ of a 0.8M sulphuric acid solution? What mass of acid is in this solution?

13.8 Stoichiometric calculations

Stoichiometry is the study and calculation of relationships between reactants and products of chemical reactions. Chapter 12 showed how to write balanced chemical equations. By knowing the ratios of substances in a reaction, it is possible to use stoichiometry to calculate the amount of reactants and products that are involved in the reaction. Some examples are shown below.



Worked Example 71: Stoichiometric calculation 1

Question: What volume of oxygen at S.T.P. is needed for the complete combustion of $2dm^3$ of propane (C₃H₈)? (Hint: CO₂ and H₂O are the products in this reaction)

Answer

Step 1 : Write a balanced equation for the reaction.

 $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

Step 2 : Determine the ratio of oxygen to propane that is needed for the reaction.

From the balanced equation, the ratio of oxygen to propane in the reactants is 5:1.

Step 3 : Determine the volume of oxygen needed for the reaction.

1 volume of propane needs 5 volumes of oxygen, therefore 2 dm³ of propane will need 10 dm³ of oxygen for the reaction to proceed to completion.



Worked Example 72: Stoichiometric calculation 2

Question: What mass of iron (II) sulphide is formed when 5.6 g of iron is completely reacted with sulfur?

Answer

Step 1 : Write a balanced chemical equation for the reaction.

$$Fe(s) + S(s) \rightarrow FeS(s)$$

Step 2 : Calculate the number of moles of iron that react.

$$n = \frac{m}{M} = \frac{5.6}{55.85} = 0.1 mol$$

Step 3 : Determine the number of moles of FeS produced.

From the equation 1 mole of Fe gives 1 mole of FeS. Therefore, 0.1 moles of iron in the reactants will give 0.1 moles of iron sulfide in the product.

Step 4 : Calculate the mass of iron sulfide formed

 $m = n \times M = 0.1 \times 87.911 = 8.79g$

The mass of iron (II) sulfide that is produced during this reaction is 8.79 g.



Important:

A closer look at the previous worked example shows that 5.6 g of iron is needed to produce 8.79 g of iron (II) sulphide. The amount of sulfur that is needed in the reactants is 3.2 g. What would happen if the amount of sulfur in the reactants was increased to 6.4 g but the amount of iron was still 5.6 g? Would more FeS be produced? In fact, the amount of iron(II) sulfide produced remains the same. No matter how much sulfur is added to the system, the amount of iron (II) sulfide will not increase because there is not enough iron to react with the additional sulfur in the reactants to produce more FeS. When all the iron is used up the reaction stops. In this example, the iron is called the **limiting reagent**. Because there is more sulfur than can be used up in the reaction, it is called the **excess reagent**.



Worked Example 73: Industrial reaction to produce fertiliser

Question: Sulfuric acid (H_2SO_4) reacts with ammonia (NH_3) to produce the fertiliser ammonium sulphate $((NH_4)_2SO_4)$ according to the following equation:

$$H_2SO_4(aq) + 2NH_3(g) \rightarrow (NH_4)_2SO_4(aq)$$

What is the maximum mass of ammonium sulphate that can be obtained from 2.0 kg of sulfuric acid and 1.0 kg of ammonia?

Answer

Step 1 : Convert the mass of sulfuric acid and ammonia into moles

$$n(H_2SO_4) = \frac{m}{M} = \frac{2000g}{98.078g/mol} = 20.39mol$$
$$n(NH_3) = \frac{1000g}{17.03g/mol} = 58.72mol$$

Step 2 : Use the balanced equation to determine which of the reactants is limiting.

From the balanced chemical equation, 1 mole of H_2SO_4 reacts with 2 moles of NH_3 to give 1 mole of $(NH_4)_2SO_4$. Therefore 20.39 moles of H_2SO_4 need to react with 40.78 moles of NH_3 . In this example, NH_3 is in excess and H_2SO_4 is the limiting reagent.

Step 3 : Calculate the maximum amount of ammonium sulphate that can be produced

Again from the equation, the mole ratio of H_2SO_4 in the reactants to $(NH_4)_2SO_4$ in the product is 1:1. Therefore, 20.39 moles of H_2SO_4 will produce 20.39 moles of $(NH_4)_2SO_4$.

The maximum mass of ammonium sulphate that can be produced is calculated as follows:

 $m = n \times M = 20.41 mol \times 132 g/mol = 2694 g$

The maximum amount of ammonium sulphate that can be produced is 2.694 kg.

?

Exercise: Stoichiometry

1. Diborane, B_2H_6 , was once considered for use as a rocket fuel. The combustion reaction for diborane is:

$$B_2H_6(g) + 3O_2(l) \rightarrow 2HBO_2(g) + 2H_2O(l)$$

If we react 2.37 grams of diborane, how many grams of water would we expect to produce?

2. Sodium azide is a commonly used compound in airbags. When triggered, it has the following reaction:

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

If 23.4 grams of sodium azide are reacted, how many moles of nitrogen gas would we expect to produce?

- 3. Photosynthesis is a chemical reaction that is vital to the existence of life on Earth. During photosynthesis, plants and bacteria convert carbon dioxide gas, liquid water, and light into glucose $(C_6H_{12}O_6)$ and oxygen gas.
 - (a) Write down the equation for the photosynthesis reaction.
 - (b) Balance the equation.
 - (c) If 3 moles of carbon dioxide are used up in the photosynthesis reaction, what mass of glucose will be produced?

13.9 Summary

- It is important to be able to quantify the changes that take place during a chemical reaction.
- The mole (n) is a SI unit that is used to describe an amount of substance that contains the same number of particles as there are atoms in 12 g of carbon.
- The number of particles in a mole is called the **Avogadro constant** and its value is 6.023 $\times 10^{23}$. These particles could be atoms, molecules or other particle units, depending on the substance.
- The **molar mass (M)** is the mass of one mole of a substance and is measured in grams per mole or g.mol⁻¹. The numerical value of an element's molar mass is the same as its relative atomic mass. For a compound, the molar mass has the same numerical value as the molecular mass of that compound.
- The relationship between moles (n), mass in grams (m) and molar mass (M) is defined by the following equation:

$$n = \frac{m}{M}$$

- In a balanced chemical equation, the number in front of the chemical symbols describes the mole ratio of the reactants and products.
- The empirical formula of a compound is an expression of the relative number of each type of atom in the compound.
- The **molecular formula** of a compound describes the actual number of atoms of each element in a molecule of the compound.
- The formula of a substance can be used to calculate the **percentage by mass** that each element contributes to the compound.
- The percentage composition of a substance can be used to deduce its chemical formula.
- One mole of gas occupies a volume of 22.4 dm³.
- The concentration of a solution can be calculated using the following equation,

$$C = \frac{n}{V}$$

where C is the concentration (in mol.dm⁻³), n is the number of moles of solute dissolved in the solution and V is the volume of the solution (in dm³).

- Molarity is a measure of the concentration of a solution, and its units are mol.dm⁻³.
- **Stoichiometry**, the study of the relationships between reactants and products, can be used to determine the quantities of reactants and products that are involved in chemical reactions.

- A **limiting reagent** is the chemical that is used up first in a reaction, and which therefore determines how far the reaction will go before it has to stop.
- An **excess reagent** is a chemical that is in greater quantity than the limiting reagent in the reaction. Once the reaction is complete, there will still be some of this chemical that has not been used up.

Exercise: Summary Exercise

- 1. Write only the word/term for each of the following descriptions:
 - (a) the mass of one mole of a substance
 - (b) the number of particles in one mole of a substance
- 2. Multiple choice: Choose the one correct answer from those given.
 - A 5 g of magnesium chloride is formed as the product of a chemical reaction. Select the **true** statement from the answers below:
 - i. 0.08 moles of magnesium chloride are formed in the reaction
 - ii. the number of atoms of Cl in the product is approximately 0.6023 \times 10^{23}
 - iii. the number of atoms of Mg is 0.05
 - iv. the atomic ratio of Mg atoms to Cl atoms in the product is 1:1
 - B 2 moles of oxygen gas react with hydrogen. What is the mass of oxygen in the reactants?
 - i. 32 g
 - ii. 0.125 g
 - iii. 64 g
 - iv. 0.063 g
 - C In the compound potassium sulphate (K $_2SO_4),$ oxygen makes up x% of the mass of the compound. x = ...
 - i. 36.8
 - ii. 9.2
 - iii. 4
 - iv. 18.3
 - D The molarity of a 150 cm³ solution, containing 5 g of NaCl is...
 - i. 0.09 M
 - ii. 5.7 imes 10 $^{-4}$ M
 - iii. 0.57 M
 - iv. 0.03 M
- 3. 300 cm^3 of a 0.1 mol.dm⁻³ solution of sulfuric acid is added to 200 cm³ of a 0.5 mol.dm⁻³ solution of sodium hydroxide.
 - a Write down a balanced equation for the reaction which takes place when these two solutions are mixed.
 - b Calculate the number of moles of sulfuric acid which were added to the sodium hydroxide solution.
 - c Is the number of moles of sulfuric acid enough to fully neutralise the sodium hydroxide solution? Support your answer by showing all relevant calculations.
 - (IEB Paper 2 2004)
- 4. Ozone (O_3) reacts with nitrogen monoxide gas (NO) to produce NO_2 gas. The NO gas forms largely as a result of emissions from the exhausts of motor vehicles and from certain jet planes. The NO_2 gas also causes the brown smog (smoke and fog), which is seen over most urban areas. This gas is also harmful to humans, as it causes breathing (respiratory) problems. The following equation indicates the reaction between ozone and nitrogen monoxide:

$$O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$$

In one such reaction 0.74 g of O_3 reacts with 0.67 g NO.

- a Calculate the number of moles of O_3 and of NO present at the start of the reaction.
- b Identify the limiting reagent in the reaction and justify your answer.
- c Calculate the mass of NO₂ produced from the reaction.

(DoE Exemplar Paper 2, 2007)

- A learner is asked to make 200 cm³ of sodium hydroxide (NaOH) solution of concentration 0.5 mol.dm⁻³.
 - a Determine the mass of sodium hydroxide pellets he needs to use to do this.
 - b Using an accurate balance the learner accurately measures the correct mass of the NaOH pellets. To the pellets he now adds exactly 200 cm³ of pure water. Will his solution have the correct concentration? Explain your answer.

300 cm³ of a 0.1 mol.dm⁻³ solution of sulfuric acid (H₂SO₄) is added to 200 cm³ of a 0.5 mol.dm⁻³ solution of NaOH at 25^{0} C.

- c Write down a balanced equation for the reaction which takes place when these two solutions are mixed.
- d Calculate the number of moles of $\mathsf{H}_2\mathsf{SO}_4$ which were added to the NaOH solution.
- e Is the number of moles of H_2SO_4 calculated in the previous question enough to fully neutralise the NaOH solution? Support your answer by showing all the relevant calculations. (IEB Paper 2, 2004)

Chapter 14

Energy Changes In Chemical Reactions - Grade 11

All chemical reactions involve energy changes. In some reactions, we are able to see these energy changes by either an increase or a decrease in the overall energy of the system.

14.1 What causes the energy changes in chemical reactions?

When a chemical reaction occurs, bonds in the reactants *break*, while new bonds *form* in the product. The following example may help to explain this.

Hydrogen reacts with oxygen to form water, according to the following equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

In this reaction, the bond between the two hydrogen atoms in the H_2 molecule will *break*, as will the bond between the oxygen atoms in the O_2 molecule. New bonds will *form* between the two hydrogen atoms and the single oxygen atom in the water molecule that is formed as the product.

For bonds to *break*, energy must be *absorbed*. When new bonds *form*, energy is *released*. The energy that is needed to break a bond is called the **bond energy** or **bond dissociation energy**. Bond energies are measured in units of $kJ.mol^{-1}$.



Definition: Bond energy

Bond energy is a measure of bond strength in a chemical bond. It is the amount of energy (in $kJ.mol^{-1}$) that is needed to break the chemical bond between two atoms.

14.2 Exothermic and endothermic reactions

In some reactions, the energy that must be *absorbed* to break the bonds in the reactants, is less than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy is *released* as either heat or light. This type of reaction is called an **exothermic** reaction. Another way of describing an exothermic reaction is that it is one in which the energy of the product is less than the energy of the reactants, because energy has been released during the reaction. We can represent this using the following general formula:



14.2

Definition: Exothermic reaction

An exothermic reaction is one that releases energy in the form of heat or light.

In other reactions, the energy that must be *absorbed* to break the bonds in the reactants, is more than the total energy that is *released* when new bonds are formed. This means that in the overall reaction, energy must be *absorbed* from the surroundings. This type of reaction is known as an **endothermic** reaction. Another way of describing an endothermic reaction is that it is one in which the energy of the product is greater than the energy of the reactants, because energy has been absorbed during the reaction. This can be represented by the following formula:

 $Reactants + Energy \rightarrow Product$



Definition: Endothermic reaction An endothermic reaction is one that absorbs energy in the form of heat.

The difference in energy (E) between the reactants and the products is known as the **heat of the reaction**. It is also sometimes referred to as the **enthalpy change** of the system.

Activity :: Demonstration : Endothermic and exothermic reactions 1 Apparatus and materials:

You will need citric acid, sodium bicarbonate, a glass beaker, the lid of an icecream container, thermometer, glass stirring rod and a pair of scissors. Note that citric acid is found in citrus fruits such as lemons. Sodium bicarbonate is actually bicarbonate of soda (baking soda), the baking ingredient that helps cakes to rise. **Method:**

- 1. Cut a piece of plastic from the ice-cream container lid that will be big enough to cover the top of the beaker. Cut a small hole in the centre of this piece of plastic and place the thermometer through it.
- 2. Pour some citric acid $(H_3C_6H_5O_7)$ into the glass beaker, cover the beaker with its 'lid' and record the temperature of the solution.
- 3. Stir in the sodium bicarbonate (NaHCO₃), then cover the beaker again.
- 4. Immediately record the temperature, and then take a temperature reading every two minutes after that. Record your results in a table like the one below.

Time (mins)	0	2	4	6
Temperature (⁰ C)				

The equation for the reaction that takes place is:

 $H_3C_6H_5O_7(aq) + 3NaHCO_3(s) \rightarrow 3CO_2(g) + 3H_2O(l) + NaC_6H_5O_7(aq)$

Results:

- Plot your temperature results on a graph of temperature against time. What happens to the temperature during this reaction?
- Is this an exothermic or an endothermic reaction?
- Why was it important to keep the beaker covered with a lid?
- Do you think a glass beaker is the best thing to use for this experiment? Explain your answer.
- Suggest another container that could have been used and give reasons for your choice. It might help you to look back to chapter **??** for some ideas!

Activity :: Demonstration : Endothermic and exothermic reactions 2 Apparatus and materials:

Vinegar, steel wool, thermometer, glass beaker and plastic lid (from previous demonstration).

Method:

- 1. Put the thermometer through the plastic lid, cover the beaker and record the temperature in the empty beaker. You will need to leave the thermometer in the beaker for about 5 minutes in order to get an accurate reading.
- 2. Take the thermometer out of the jar.
- 3. Soak a piece of steel wool in vinegar for about a minute. The vinegar removes the protective coating from the steel wool so that the metal is exposed to oxygen.
- 4. After the steel wool has been in the vinegar, remove it and squeeze out any vinegar that is still on the wool. Wrap the steel wool around the thermometer and place it (still wrapped round the thermometer) back into the jar. The jar is automatically sealed when you do this because the thermometer is through the top of the lid.
- 5. Leave the steel wool in the beaker for about 5 minutes and then record the temperature. Record your observations.

Results:

You should notice that the temperature *increases* when the steel wool is wrapped around the thermometer.

Conclusion:

The reaction between oxygen and the exposed metal in the steel wool, is **exother**-**mic**, which means that energy is released and the temperature increases.

14.3 The heat of reaction

The **heat of the reaction** is represented by the symbol ΔH , where:

$$\Delta H = E_{prod} - E_{react}$$

 In an exothermic reaction, ΔH is less than zero because the energy of the reactants is greater than the energy of the product. For example,

 $H_2 + Cl_2 \rightarrow 2HCl \ \Delta H = -183 \text{ kJ}$

• In an *endothermic* reaction, ΔH is greater than zero because the energy of the reactants is less than the energy of the product. For example,

 $C+H_2O\rightarrow CO+H_2~\Delta {\rm H}=+131~{\rm kJ}$

Some of the information relating to exothermic and endothermic reactions is summarised in table 14.1.

ruble 1111. / comparison of exemicinite and endothermite reactions					
Type of reaction	Exothermic	Endothermic			
Energy absorbed or re-	Released	Absorbed			
leased					
Relative energy of reac-	Energy of reactants greater	Energy of reactants less			
tants and products	than energy of product	than energy of product			
Sign of ΔH	Negative	Positive			

Table 14.1: A comparison of exothermic and endothermic reactions



14.3

Definition: Enthalpy

Enthalpy is the heat content of a chemical system, and is given the symbol 'H'.

Important: Writing equations using ΔH

There are two ways to write the heat of the reaction in an equation For the exothermic reaction $C(s) + O_2(g) \rightarrow CO_2(g)$, we can write:

 $C(s)+O_2(g)\to CO_2(g)$ $\Delta {\rm H}=-393~{\rm kJ.mol^{-1}}$ or $C(s)+O_2(g)\to CO_2(g)+393~{\rm kJ.mol^{-1}}$

For the endothermic reaction, $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$, we can write:

 $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g) \Delta H = +131 \text{ kJ.mol}^{-1} \text{ or}$ $C(s) + H_2O(g) + 131 \text{ kJ.mol}^{-1} \rightarrow CO + H_2$

The **units** for ΔH are kJ.mol⁻¹. In other words, the ΔH value gives the amount of energy that is absorbed or released per mole of product that is formed. Units can also be written as kJ, which then gives the total amount of energy that is released or absorbed when the product forms.

Activity :: Investigation : Endothermic and exothermic reactions Apparatus and materials:

Approximately 2 g each of calcium chloride (CaCl₂), sodium hydroxide (NaOH), potassium nitrate (KNO₃) and barium chloride (BaCl₂); concentrated sulfuric acid (H₂SO₄); 5 test tubes; thermometer.

Method:

- 1. Dissolve about 1 g of each of the following substances in 5-10 cm³ of water in a test tube: CaCl₂, NaOH, KNO₃ and BaCl₂.
- 2. Observe whether the reaction is endothermic or exothermic, either by feeling whether the side of the test tube gets hot or cold, or using a thermometer.
- Dilute 3 cm³ of concentrated H₂SO₄ in 10 cm³ of water in the fifth test tube and observe whether the temperature changes.
- 4. Wait a few minutes and then add NaOH to the H_2SO_4 . Observe any energy changes.
- 5. Record which of the above reactions are endothermic and which are exothermic.

Results:

- When BaCl₂ and KNO₃ dissolve in water, they take in heat from the surroundings. The dissolution of these salts is **endothermic**.
- When CaCl₂ and NaOH dissolve in water, heat is released. The process is exothermic.

• The reaction of H₂SO₄ and NaOH is also exothermic.

14.4 Examples of endothermic and exothermic reactions

There are many examples of endothermic and exothermic reactions that occur around us all the time. The following are just a few examples.

1. Endothermic reactions

• Photosynthesis

Photosynthesis is the chemical reaction that takes place in plants, which uses energy from the sun to change carbon dioxide and water into food that the plant needs to survive, and which other organisms (such as humans and other animals) can eat so that they too can survive. The equation for this reaction is:

 $6CO_2 + 12H_2O + energy \rightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$

Photosynthesis is an endothermic reaction because it will not happen without an external source of energy, which in this case is sunlight.

• The thermal decomposition of limestone

In industry, the breakdown of limestone into quicklime and carbon dioxide is very important. Quicklime can be used to make steel from iron and also to neutralise soils that are too acid. However, the limestone must be heated in a kiln at a temperature of over 900^0C before the decomposition reaction will take place. The equation for the reaction is shown below:

$$CaCO_3 \rightarrow CaO + CO_2$$

2. Exothermic reactions

• **Combustion reactions** - The burning of fuel is an example of a combustion reaction, and we as humans rely heavily on this process for our energy requirements. The following equations describe the combustion of a hydrocarbon such as *methane* (CH₄):

$$\label{eq:Fuel} \begin{split} \mathrm{Fuel} + \mathrm{Oxygen} & \rightarrow \mathrm{Heat} + \mathrm{Water} + \mathrm{CarbonDioxide} \\ \mathrm{CH}_4 + \mathrm{2O}_2 & \rightarrow \mathrm{Heat} + \mathrm{H_2O} + \mathrm{CO}_2 \end{split}$$

This is why we burn fuels for energy, because the chemical changes that take place during the reaction release huge amounts of energy, which we then use for things like power and electricity. You should also note that *carbon dioxide* is produced during this reaction. Later we will discuss some of the negative impacts of CO_2 on the environment. The chemical reaction that takes place when fuels burn therefore has both positive and negative consequences.

• Respiration

Respiration is the chemical reaction that happens in our bodies to produce energy for our cells. The equation below describes what happens during this reaction:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy$$

In the reaction above, glucose (a type of carbohydrate in the food we eat) reacts with oxygen from the air that we breathe in, to form carbon dioxide (which we breathe out), water and energy. The energy that is produced allows the cell to carry out its functions efficiently. Can you see now why you are always told that you must eat food to get energy? It is not the food itself that provides you with energy, but the exothermic reaction that takes place when compounds within the food react with the oxygen you have breathed in!

Intering Fac

14.5

Lightsticks or glowsticks are used by divers, campers, and for decoration and fun. A lightstick is a plastic tube with a glass vial inside it. To activate a lightstick, you bend the plastic stick, which breaks the glass vial. This allows the chemicals that are inside the glass to mix with the chemicals in the plastic tube. These two chemicals react and release energy. Another part of a lightstick is a fluorescent dye which changes this energy into light, causing the lightstick to glow!



Exercise: Endothermic and exothermic reactions

- 1. In each of the following reactions, say whether the reaction is endothermic or exothermic, and give a reason for your answer.
 - (a) $H_2 + I_2 \rightarrow 2HI + 21kJ$
 - (b) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \Delta H = -802 \text{ kJ}$
 - (c) The following reaction takes place in a flask: Ba(OH)₂.8H₂O + 2NH₄NO₃ → Ba(NO₃)₂ + 2NH₃ + 10H₂O Within a few minutes, the temperature of the flask drops by approximately 20C.
 - (d) $Na + Cl_2 \rightarrow 2NaCl \Delta H = -411 \text{ kJ}$
 - (e) $C + O_2 \rightarrow CO_2$
- 2. For each of the following descriptions, say whether the process is endothermic or exothermic and give a reason for your answer.
 - (a) evaporation
 - (b) the combustion reaction in a car engine
 - (c) bomb explosions
 - (d) melting ice
 - (e) digestion of food
 - (f) condensation

14.5 Spontaneous and non-spontaneous reactions

Activity :: Demonstration : Spontaneous and non-spontaneous reactions Apparatus and materials:

A length of magnesium ribbon, thick copper wire and a bunsen burner



Method:

- 1. Scrape the length of magnesium ribbon and copper wire clean.
- 2. Heat each piece of metal over the bunsen burner, in a non-luminous flame. Observe whether any chemical reaction takes place.
- 3. Remove the metals from the flame and observe whether the reaction stops. If the reaction stops, return the metal to the bunsen flame and continue to heat it.

Results:

- Did any reaction take place before the metals were heated?
- Did either of the reactions continue after they were removed from the flame?
- Write a balanced equation for each of the chemical reactions that takes place.

In the demonstration above, the reaction between magnesium and oxygen, and the reaction between copper and oxygen are both **non-spontaneous**. Before the metals were held over the bunsen burner, no reaction was observed. They need energy to *initiate* the reaction. After the reaction has started, it may then carry on spontaneously. This is what happened when the magnesium reacted with oxygen. Even after the magnesium was removed from the flame, the reaction continued. Other reactions will not carry on unless there is a constant addition of energy. This was the case when copper reacted with oxygen. As soon as the copper was removed from the flame, the flame, the reaction stopped.

Now try adding a solution of dilute sulfuric acid with a solution of sodium hydroxide. What do you observe? This is an example of a **spontaneous reaction** because the reaction takes place without any energy being added.



Definition: Spontaneous reaction

A spontaneous reaction is a physical or chemical change that occurs without the addition of energy.

14.6 Activation energy and the activated complex

From the demonstrations of spontaneous and non-spontaneous reactions, it should be clear that most reactions will not take place until the system has some minimum amount of energy added

to it. This energy is called the **activation energy**. **Activation energy** is the 'threshold energy' or the energy that must be overcome in order for a chemical reaction to occur.



Definition: Activation energy

Activation energy or 'threshold energy' is the energy that must be overcome in order for a chemical reaction to occur.

It is possible to draw an energy diagram to show the energy changes that take place during a particular reaction. Let's consider an example:



Figure 14.1: The energy changes that take place during an exothermic reaction

The reaction between $H_2(g)$ and $F_2(g)$ (figure 14.1) needs energy in order to proceed, and this is the activation energy. Once the reaction has started, an in-between, temporary state is reached where the two reactants combine to give H_2F_2 . This state is sometimes called a **transition state** and the energy that is needed to reach this state is equal to the activation energy for the reaction. The compound that is formed in this transition state is called the **activated complex**. The transition state lasts for only a very short time, after which either the original bonds reform, or the bonds are broken and a new product forms. In this example, the final product is HF and it has a lower energy than the reactants. The reaction is exothermic and ΔH is negative.



Definition: Activated complex

The activated complex is a transitional structure in a chemical reaction that results from the effective collisions between reactant molecules, and which remains while old bonds break and new bonds form.

In endothermic reactions, the final products have a higher energy than the reactants. An energy diagram is shown below (figure 14.2) for the endothermic reaction $XY + Z \rightarrow X + YZ$. In this example, the activated complex has the formula XYZ. Notice that the activation energy for the endothermic reaction is much greater than for the exothermic reaction.



The reaction between H and F was considered by NASA (National Aeronautics and Space Administration) as a fuel system for rocket boosters because of the energy that is released during this exothermic reaction.



Time→

Figure 14.2: The energy changes that take place during an endothermic reaction

Important: Enzymes and activation energy

An enzyme is a catalyst that helps to speed up the rate of a reaction by lowering the activation energy of a reaction. There are many enzymes in the human body, without which lots of important reactions would never take place. Cellular respiration is one example of a reaction that is catalysed by enzymes. You will learn more about catalysts in chapter **??**.

?

Exercise: Energy and reactions

1. Carbon reacts with water according to the following equation:

 $C + H_2O \Leftrightarrow CO + H_2 \Delta H > 0$

- (a) Is this reaction endothermic or exothermic?
- (b) Give a reason for your answer.
- 2. Refer to the graph below and then answer the questions that follow:



- (a) What is the energy of the reactants?
- (b) What is the energy of the products?
- (c) Calculate ΔH .
- (d) What is the activation energy for this reaction?

14.7 Summary

- When a reaction occurs, some bonds break and new bonds form. These changes involve energy.
- When bonds break, energy is absorbed and when new bonds form, energy is released.
- The **bond energy** is the amount of energy that is needed to break the chemical bond between two atoms.
- If the energy that is needed to *break* the bonds is greater than the energy that is released when new bonds *form*, then the reaction is **endothermic**. The energy of the product is greater than the energy of the reactants.
- If the energy that is needed to *break* the bonds is less than the energy that is released when new bonds *form*, then the reaction is **exothermic**. The energy of the product is less than the energy of the reactants.
- An endothermic reaction is one that **absorbs** energy in the form of heat, while an exothermic reaction is one that **releases** energy in the form of heat and light.
- The difference in energy between the reactants and the product is called the **heat of** reaction and has the symbol ΔH .
- In an endothermic reaction, ΔH is a positive number, and in an exothermic reaction, ΔH will be negative.
- Photosynthesis, evaporation and the thermal decomposition of limestone, are all examples
 of endothermic reactions.
- Combustion reactions and respiration are both examples of exothermic reactions.
- A reaction which proceeds without additional energy being added, is called a spontaneous reaction.
- Reactions where energy must be *supplied* for the activation energy to be overcome, are called **non-spontaneous** reactions.
- In any reaction, some minimum energy must be overcome before the reaction will proceed. This is called the activation energy of the reaction.
- The **activated complex** is the transitional product that is formed during a chemical reaction while old bonds break and new bonds form.

Exercise: Summary Exercise

- 1. For each of the following, say whether the statement is **true** or **false**. If it is false, give a reason for your answer.
 - (a) Energy is released in all chemical reactions.
 - (b) The condensation of water vapour is an example of an endothermic reaction.

- (c) In an exothermic reaction ΔH is less than zero.
- (d) All non-spontaneous reactions are endothermic.
- 2. For each of the following, choose the one correct answer.
 - (a) For the following reaction:

$$A + B \Leftrightarrow AB \ \Delta H = -129 \ kJ.mol^{-1}$$

- $\ensuremath{\text{i.}}$ The energy of the reactants is less than the energy of the product.
- ii. The energy of the product is less than the energy of the reactants.
- iii. The reaction is non-spontaneous.
- iv. The overall energy of the system increases during the reaction.
- (b) Consider the following chemical equilibrium:

$$2NO_2 \Leftrightarrow N_2O_4$$

Which one of the following graphs best represents the changes in potential energy that take place during the production of N_2O_4 ?



3. The cellular respiration reaction is catalysed by enzymes. The equation for the reaction is:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

The change in potential energy during this reaction is shown below:



- (a) Will the value of ΔH be positive or negative? Give a reason for your answer.
- (b) Explain what is meant by 'activation energy'.
- (c) What role do enzymes play in this reaction?
- (d) Glucose is one of the reactants in cellular respiration. What important chemical reaction produces glucose?
- (e) Is the reaction in your answer above an endothermic or an exothermic one? Explain your answer.
- (f) Explain why proper nutrition and regular exercise are important in maintaining a healthy body.

Chapter 15

Types of Reactions - Grade 11

There are many different types of chemical reactions that can take place. In this chapter, we will be looking at a few of the more common reaction types: acid-base and acid-carbonate reactions, redox reactions and addition, elimination and substitution reactions.

15.1 Acid-base reactions

15.1.1 What are acids and bases?

In our daily lives, we encounter many examples of acids and bases. In the home, vinegar (acetic acid), lemon juice (citric acid) and tartaric acid (the main acid found in wine) are common, while hydrochloric acid, sulfuric acid and nitric acid are examples of acids that are more likely to be found in laboratories and industry. Hydrochloric acid is also found in the gastric juices in the stomach. Even fizzy drinks contain acid (carbonic acid), as do tea and wine (tannic acid)! Bases that you may have heard of include sodium hydroxide (caustic soda), ammonium hydroxide and ammonia. Some of these are found in household cleaning products. Acids and bases are also important commercial products in the fertiliser, plastics and petroleum refining industries. Some common acids and bases, and their chemical formulae, are shown in table 15.1.

Acid	Formula	Base	Formula
Hydrochoric acid	HCI	Sodium hydroxide	NaOH
Sulfuric acid	H_2SO_4	Potassium hydroxide	КОН
Nitric acid	HNO ₃	Sodium carbonate	Na_2CO_3
Acetic (ethanoic) acid	CH ₃ COOH	Calcium hydroxide	$Ca(OH)_2$
Carbonic acid	H_2CO_3	Magnesium hydroxide	$Mg(OH)_2$
Sulfurous acid	H_2SO_3	Ammonia	NH_3
Phosphoric acid	H_3PO_4	Sodium bicarbonate	$NaHCO_3$

Table 15.1: Some common acids and bases and their chemical formulae

Most acids share certain characteristics, and most bases also share similar characteristics. It is important to be able to have a definition for acids and bases so that they can be correctly identified in reactions.

15.1.2 Defining acids and bases

A number of definitions for acids and bases have developed over the years. One of the earliest was the **Arrhenius** definition. Arrhenius (1887) noticed that water dissociates (splits up) into hydronium (H_3O^+) and hydroxide (OH^-) ions according to the following equation:

$$H_2O \Leftrightarrow H_3O^+ + OH^-$$

267

Arrhenius described an acid as a compound that increases the concentration of H_3O^+ ions in solution, and a base as a compound that increases the concentration of OH^- ions in a solution. Look at the following examples showing the dissociation of hydrochloric acid and sodium hydroxide (a base) respectively:

more information dissociation, refer to chapter 20.

For

on

1. $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

Hydrochloric acid in water increases the concentration of H_3O^+ ions and is therefore an acid.

2. $NaOH + H_2O \rightarrow Na^+ + OH^-$

Sodium hydroxide in water increases the concentration of OH⁻ ions and is therefore a base.

However, this definition could only be used for acids and bases in water. It was important to come up with a much broader definition for acids and bases.

It was Lowry and Bronsted (1923) who took the work of Arrhenius further to develop a broader definition for acids and bases. The Bronsted-Lowry model defines acids and bases in terms of their ability to donate or accept protons.



Definition: Acids and bases

According to the Bronsted-Lowry theory of acids and bases, an acid is a substance that gives away protons (H^+) , and is therefore called a **proton donor**. A **base** is a substance that takes up protons, and is therefore called a proton acceptor.

Below are some examples:

1.
$$HCl(g) + NH_3(g) \rightarrow NH^{4+} + Cl^{-1}$$

In order to decide which substance is a proton donor and which is a proton acceptor, we need to look at what happens to each reactant. The reaction can be broken down as follows:

 $HCl \rightarrow Cl^- + H^+$ and $\rm NH_3 + H^+ \rightarrow \rm NH_4^+$

From these reactions, it is clear that HCl is a proton donor and is therefore an acid, and that NH_3 is a proton acceptor and is therefore a **base**.

2. $CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$

The reaction can be broken down as follows:

 $CH_3COOH \rightarrow CH_3COO^- + H^+$ and $H_2O + H^+ \rightarrow H_3O^+$

In this reaction, CH_3COOH (acetic acid) is a proton donor and is therefore the acid. In this case, water acts as a base because it accepts a proton to form H_3O^+ .

3. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

The reaction can be broken down as follows:

 ${\rm H}_2 O \rightarrow O H^- + H^+$ and ${\rm NH}_3 + H^+ \rightarrow {\rm NH}_4^+$

In this reaction, water donates a proton and is therefore an **acid** in this reaction. Ammonia accepts the proton and is therefore the **base**. Notice that in the previous equation, water acted as a base and that in this equation it acts as an acid. Water can act as both an acid and a base depending on the reaction. This is also true of other substances. These substances are called **ampholytes** and are said to be **amphoteric**.



Definition: Amphoteric

An amphoteric substance is one that can react as either an acid or base. Examples of amphoteric substances include water, zinc oxide and beryllium hydroxide.

15.1.3 Conjugate acid-base pairs

Look at the reaction between hydrochloric acid and ammonia to form ammonium and chloride ions:

$$HCl + NH_3 \Leftrightarrow NH_4^+ + Cl^-$$

Looking firstly at the *forward reaction* (i.e. the reaction that proceeds from *left* to *right*), the changes that take place can be shown as follows:

$$HCl \rightarrow Cl^- + H^+$$
 and
 $NH_3 + H^+ \rightarrow NH_4^+$

Looking at the *reverse reaction* (i.e. the reaction that proceeds from *right* to *left*), the changes that take place are as follows:

 $\rm NH_4^+ \rightarrow \rm NH_3 + H^+$ and $\rm Cl^- + H^+ \rightarrow \rm HCl$

In the **forward reaction**, HCl is a proton donor (acid) and NH₃ is a proton acceptor (base). In the **reverse reaction**, the chloride ion is the proton acceptor (base) and NH₄⁺ is the proton donor (acid). A **conjugate acid-base pair** is two compounds in a reaction that change into each other through the loss or gain of a proton. The conjugate acid-base pairs for the above reaction are shown below.



The reaction between ammonia and water can also be used as an example:





Definition: Conjugate acid-base pair

The term refers to two compounds that transform into each other by the gain or loss of a proton.



Exercise: Acids and bases

- 1. In the following reactions, identify (1) the acid and the base in the reactants and (2) the salt in the product.
 - (a) $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$
 - (b) $CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O_4$
 - (c) $H_2O + C_6H_5OH \rightarrow H_3O^+ + C_6H_5O^-$
 - (d) $HBr + C_5H_5N \rightarrow (C_5H_5NH^+)Br^-$
- 2. In each of the following reactions, label the conjugate acid-base pairs.
 - (a) $H_2SO_4 + H_2O \Leftrightarrow H_3O^+ + HSO_4^-$
 - (b) $NH_4^+ + F^- \Leftrightarrow HF + NH_3$
 - (c) $H_2O + CH_3COO^- \Leftrightarrow CH_3COOH + OH^-$
 - (d) $H_2SO_4 + Cl^- \Leftrightarrow HCl + HSO_4^-$

15.1.4 Acid-base reactions

When an acid and a base react, they neutralise each other to form a **salt**. If the base contains hydroxide (OH^-) ions, then *water* will also be formed. The word *salt* is a general term which applies to the products of all acid-base reactions. A salt is a product that is made up of the cation from a base and the anion from an acid. When an acid reacts with a base, they **neutralise** each other. In other words, the acid becomes less acidic and the base becomes less basic. Look at the following examples:

1. Hydrochloric acid reacts with sodium hydroxide to form sodium chloride (the salt) and water. Sodium chloride is made up of Na⁺ cations from the base (NaOH) and Cl⁻ anions from the acid (HCl).

 $\rm HCl + NaOH \rightarrow \rm H_2O + NaCl$

2. Hydrogen bromide reacts with potassium hydroxide to form potassium bromide (the salt) and water. Potassium bromide is made up of K⁺ cations from the base (KOH) and Br⁻ anions from the acid (HBr).

 $\mathrm{HBr} + \mathrm{KOH} \rightarrow \mathrm{H_2O} + \mathrm{KBr}$

3. Hydrochloric acid reacts with sodium hydrocarbonate to form sodium chloride (the salt) and hydrogen carbonate. Sodium chloride is made up of Na⁺ cations from the base (NaHCO₃) and Cl⁻ anions from the acid (HCl).

 $\mathrm{HCl} + \mathrm{NaHCO}_3 \rightarrow \mathrm{H_2CO}_3 + \mathrm{NaCl}$

You should notice that in the first two examples, the base contained OH^- ions, and therefore the products were a *salt* and *water*. NaCl (table salt) and KBr are both salts. In the third example, NaHCO₃ also acts as a base, despite not having OH^- ions. A salt is still formed as one of the products, but no water is produced.

It is important to realise how important these neutralisation reactions are. Below are some examples:

• Domestic uses

Calcium oxide (CaO) is put on soil that is too acid. Powdered limestone (CaCO₃) can also be used but its action is much slower and less effective. These substances can also be used on a larger scale in farming and also in rivers.

• Biological uses

Acids in the stomach (e.g. hydrochloric acid) play an important role in helping to digest food. However, when a person has a stomach ulcer, or when there is too much acid in the stomach, these acids can cause a lot of pain. **Antacids** are taken to neutralise the acids so that they don't burn as much. Antacids are bases which neutralise the acid. Examples of antacids are aluminium hydroxide, magnesium hydroxide ('milk of magnesia') and sodium bicarbonate ('bicarbonate of soda'). Antacids can also be used to relieve heartburn.

• Industrial uses

Alkaline calcium hydroxide (limewater) can be used to absorb harmful SO_2 gas that is released from power stations and from the burning of fossil fuels.



Bee stings are acidic and have a pH between 5 and 5.5. They can be soothed by using substances such as calomine lotion, which is a mild alkali based on zinc oxide. Bicarbonate of soda can also be used. Both alkalis help to neutralise the acidic bee sting and relieve some of the itchiness!

Important: Acid-base titrations

The neutralisation reaction between an acid and a base can be very useful. If an acidic solution of known concentration (a standard solution) is added to an alkaline solution until the solution is exactly neutralised (i.e. it has neither acidic nor basic properties), it is possible to calculate the exact concentration of the unknown solution. It is possible to do this because, at the exact point where the solution is neutralised, chemically equivalent amounts of acid and base have reacted with each other. This type of calculation is called **volumetric analysis**. The process where an acid solution and a basic solution are added to each other for this purpose, is called a **titration**, and the point of neutralisation is called the **end point** of the reaction. So how exactly can a titration be carried out to determine an unknown concentration? Look at the following steps to help you to understand the process.

Step 1:

A measured volume of the solution with unknown concentration is put into a flask.

Step 2:

A suitable indicator is added to this solution (bromothymol blue and phenolpthalein are common indicators).

Step 3:

A volume of the standard solution is put into a burette and is slowly added to the solution in the flask, drop by drop.

Step 4:

At some point, adding one more drop will change the colour of the unknown solution. For example, if the solution is basic and bromothymol blue is being used as the indicator in the titration, the bromothymol blue would originally have coloured the solution blue. At the end point of the reaction, adding one more drop of acid will change the colour of the basic solution from blue to yellow. Yellow shows that the solution is now acidic.

Step 5:

Record the volume of standard solution that has been added up to this point.

Step 6:

Use the information you have gathered to calculate the exact concentration of the unknown solution. A worked example is shown below.



Important: Titration calculations

When you are busy with these calculations, you will need to remember the following:

 $1 \mbox{dm}^3 = 1$ litre = 1000 \mbox{ml} = 1000 \mbox{cm}^3 , therefore dividing \mbox{cm}^3 by 1000 will give you an answer in $\mbox{dm}^3.$

Some other terms and equations which will be useful to remember are shown below:

- Molarity is a term used to describe the concentration of a solution, and is measured in mol.dm⁻³. The symbol for molarity is M. Refer to chapter 13 for more information on molarity.
- Moles = molarity (mol.dm⁻³) x volume (dm³)
- Molarity (mol.dm⁻³) = mol / volume



Worked Example 74: Titration calculation

Question: Given the equation:

 $NaOH + HCl \rightarrow NaCl + H_2O$

 $25 \rm cm^3$ of a sodium hydroxide solution was pipetted into a conical flask and titrated with 0.2M hydrochloric acid. Using a suitable indicator, it was found that $15 \rm cm^3$ of acid was needed to neutralise the alkali. Calculate the molarity of the sodium hydroxide.

Answer

Step 1 : Write down all the information you know about the reaction, and make sure that the equation is balanced.

NaOH: V = 25 cm³ HCI: V = 15 cm³; C = 0.2 M The equation is already balanced.

Step 2 : Calculate the number of moles of HCI that react according to this equation.

$$M = \frac{n}{V}$$

Therefore, $n(HCI) = M \times V$ (make sure that all the units are correct!)

 $\label{eq:model} \begin{array}{l} {\sf M} = 0.2 {\sf mol.dm}^{-3} \\ {\sf V} = 15 {\sf cm}^3 = 0.015 {\sf dm}^3 \end{array}$

Therefore

$$n(HCl) = 0.2 \times 0.015 = 0.003$$

There are 0.003 moles of HCl that react

Step 3 : Calculate the number of moles of sodium hydroxide in the reaction Look at the equation for the reaction. For every mole of HCl there is one mole of NaOH that is involved in the reaction. Therefore, if 0.003 moles of HCl react, we can conclude that the same quantity of NaOH is needed for the reaction. The number of moles of NaOH in the reaction is 0.003.

Step 4 : Calculate the molarity of the sodium hydroxide

First convert the volume into $dm^3,\ V=0.025\ dm^3.$ Then continue with the calculation.

$$M = \frac{n}{V} = \frac{0.003}{0.025} = 0.12$$

The molarity of the NaOH solution is 0.12 mol.dm 3 or 0.12 M



Worked Example 75: Titration calculation

Question: 4.9 g of sulfuric acid is dissolved in water and the final solution has a volume of 220 cm³. Using titration, it was found that 20 cm³ of this solution was

able to completely neutralise 10 $\rm cm^3$ of a sodium hydroxide solution. Calculate the concentration of the sodium hydroxide in mol.dm^{-3}.

Answer

Step 1 : Write a balanced equation for the titration reaction. ${\rm H_2SO_4} + 2{\rm NaOH} \rightarrow {\rm Na_2SO_4} + 2{\rm H_2O}$

Step 2 : Calculate the molarity of the sulfuric acid solution.

 $\begin{array}{l} {\sf M} = {\sf n}/{\sf V} \\ {\sf V} = 220 \ {\sf cm}^3 = 0.22 \ {\sf dm}^3 \end{array}$

$$n = \frac{m}{M} = \frac{4.9g}{98g.mol^{-1}} = 0.05mols$$

Therefore,

$$M = \frac{0.05}{0.22} = 0.23 mol. dm^{-3}$$

Step 3 : Calculate the moles of sulfuric acid that were used in the neutralisation reaction.

Remember that only 20 cm^3 of the sulfuric acid solution is used.

M = n/V, therefore $n = M \times V$

 $n = 0.23 \times 0.02 = 0.0046 mol$

Step 4 : Calculate the number of moles of sodium hydroxide that were neutralised.

According to the balanced chemical equation, the mole ratio of H_2SO_4 to NaOH is 1:2. Therefore, the number of moles of NaOH that are neutralised is 0.0046 \times 2 = 0.0092 mols.

Step 5 : Calculate the concentration of the sodium hydroxide solution.

$$M = \frac{n}{V} = \frac{0.0092}{0.01} = 0.92M$$

15.1.5 Acid-carbonate reactions

Activity :: Demonstration : The reaction of acids with carbonates Apparatus and materials:

Small amounts of sodium carbonate and calcium carbonate (both in powder form); hydrochloric acid and sulfuric acid; retort stand; two test tubes; two rubber stoppers for the test tubes; a delivery tube; lime water. The demonstration should be set up as shown below.


Method:

- 1. Pour limewater into one of the test tubes and seal with a rubber stopper.
- 2. Pour a small amount of hydrochloric acid into the remaining test tube.
- 3. Add a small amount of sodium carbonate to the acid and seal the test tube with the rubber stopper.
- 4. Connect the two test tubes with a delivery tube.
- 5. Observe what happens to the colour of the limewater.
- 6. Repeat the above steps, this time using sulfuric acid and calcium carbonate.

Observations:

The clear lime water turns milky meaning that carbon dioxide has been produced.

When an acid reacts with a carbonate a salt, carbon dioxide and water are formed. Look at the following examples:

• Nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide and water.

$$2HNO_3 + Na_2CO_3 \rightarrow 2NaNO_3 + CO_2 + H_2O$$

• Sulfuric acid reacts with calcium carbonate to form calcium sulphate, carbon dioxide and water.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + CO_2 + H_2O$$

• Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide and water.

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$



Exercise: Acids and bases

1. The compound NaHCO $_3$ is commonly known as baking soda. A recipe requires 1.6 g of baking soda, mixed with other ingredients, to bake a cake.

- (a) Calculate the number of moles of NaHCO₃ used to bake the cake.
- (b) How many atoms of oxygen are there in the 1.6 g of baking soda? During the baking process, baking soda reacts with an acid to produce carbon dioxide and water, as shown by the reaction equation below:

$$\mathrm{HCO}_{3}^{-}(\mathrm{aq}) + \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{CO}_{2}(\mathrm{g}) + \mathrm{H}_{2}\mathrm{O}(\mathrm{l})$$

- (c) Identify the reactant which acts as the Bronsted-Lowry base in this reaction. Give a reason for your answer.
- (d) Use the above equation to explain why the cake rises during this baking process.

(DoE Grade 11 Paper 2, 2007)

2. Label the acid-base conjugate pairs in the following equation:

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$$

 A certain antacid tablet contains 22.0 g of baking soda (NaHCO₃). It is used to neutralise the excess hydrochloric acid in the stomach. The balanced equation for the reaction is:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

The hydrochloric acid in the stomach has a concentration of 1.0 mol.dm^{-3} . Calculate the volume of the hydrochloric acid that can be neutralised by the antacid tablet.

(DoE Grade 11 Paper 2, 2007)

- 4. A learner is asked to prepare a *standard solution* of the weak acid, oxalic acid $(COOH)_2 2H_2O$ for use in a titration. The volume of the solution must be 500 cm³ and the concentration 0.2 mol.dm⁻³.
 - (a) Calculate the mass of oxalic acid which the learner has to dissolve to make up the required standard solution. The leaner titrates this 0.2 mol.dm⁻³ oxalic acid solution against a solution of sodium hydroxide. He finds that 40 cm³ of the oxalic acid solution exactlt neutralises 35 cm³ of the sodium hydroxide solution.
 - (b) Calculate the concentration of the sodium hydroxide solution.
- A learner finds some sulfuric acid solution in a bottle labelled 'dilute sulfuric acid'. He wants to determine the concentration of the sulphuric acid solution. To do this, he decides to titrate the sulphuric acid against a standard potassium hydroxide (KOH) solution.
 - (a) What is a standard solution?
 - (b) Calculate the mass of KOH which he must use to make 300 cm 3 of a 0.2 mol.dm $^{-3}$ KOH solution.
 - (c) Calculate the pH of the 0.2 mol.dm $^{-3}$ KOH solution (assume standard temperature).
 - (d) Write a balanced chemical equation for the reaction between ${\rm H}_2{\rm SO}_4$ and KOH.
 - (e) During the titration he finds that 15 cm³ of the KOH solution neutralises 20 cm³ of the H_2SO_4 solution. Calculate the concentration of the H_2SO_4 solution.

(IEB Paper 2, 2003)

15.2 Redox reactions

A second type of reaction is the **redox** reaction, in which both **oxidation** and **reduction** take place.

15.2.1 Oxidation and reduction

If you look back to chapter 4, you will remember that we discussed how, during a chemical reaction, an exchange of electrons takes place between the elements that are involved. Using *oxidation numbers* is one way of tracking what is happening to these electrons in a reaction. Refer back to section 4.11 if you can't remember the rules that are used to give an oxidation number to an element. Below are some examples to refresh your memory before we carry on with this section!

Examples:

1. CO_2

Each oxygen atom has an oxidation number of -2. This means that the charge on *two* oxygen atoms is -4. We know that the molecule of CO_2 is neutral, therefore the carbon atom must have an oxidation number of +4.

2. **KMnO**₄

Overall, this molecule has a neutral charge, meaning that the sum of the oxidation numbers of the elements in the molecule must equal zero. Potassium (K) has an oxidation number of +1, while oxygen (O) has an oxidation number of -2. If we exclude the atom of manganese (Mn), then the sum of the oxidation numbers equals +1+(-2x4)=-7. The atom of manganese must therefore have an oxidation number of +7 in order to make the molecule neutral.

By looking at how the oxidation number of an element changes during a reaction, we can easily see whether that element is being **oxidised** or **reduced**.



Definition: Oxidation and reduction

Oxidation is the *loses* of an electron by a molecule, atom or ion. Reduction is the *gain* of an electron by a molecule, atom or ion.

Example:

$$Mg + Cl_2 \rightarrow MgCl_2$$

As a *reactant*, magnesium has an oxidation number of zero, but as part of the *product* magnesium chloride, the element has an oxidation number of +2. Magnesium has *lost* two electrons and has therefore been *oxidised*. This can be written as a **half-reaction**. The half-reaction for this change is:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

As a *reactant*, chlorine has an oxidation number of zero, but as part of the *product* magnesium chloride, the element has an oxidation number of -1. Each chlorine atom has *gained* an electron and the element has therefore been *reduced*. The half-reaction for this change is:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$



Definition: Half-reaction

A half reaction is either the oxidation or reduction reaction part of a redox reaction. A half reaction is obtained by considering the change in oxidation states of the individual substances that are involved in the redox reaction.

Important: Oxidation and reduction made easy!

An easy way to think about oxidation and reduction is to remember:

'OILRIG' - Oxidation Is Loss of electrons, Reduction Is Gain of electrons.

An element that is **oxidised** is called a **reducing agent**, while an element that is **reduced** is called an **oxidising agent**.

15.2.2 Redox reactions

F

Definition: Redox reaction

A redox reaction is one involving oxidation and reduction, where there is always a change in the oxidation numbers of the elements involved.

Activity :: Demonstration : Redox reactions Materials:

A few granules of zinc; 15 ml copper (II) sulphate solution (blue colour), glass beaker.



Method:

Add the zinc granules to the copper sulphate solution and observe what happens. What happens to the zinc granules? What happens to the colour of the solution? **Results:**

- Zinc becomes covered in a layer that looks like copper.
- The blue copper sulphate solution becomes clearer.

 Cu^{2+} ions from the $CuSO_4$ solution are **reduced** to form copper metal. This is what you saw on the zinc crystals. The reduction of the copper ions (in other words, their removal from the copper sulphate solution), also explains the change in colour of the solution. The equation for this reaction is:

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Zinc is $\boldsymbol{oxidised}$ to form Zn^{2+} ions which are clear in the solution. The equation for this reaction is:

$$\operatorname{Zn} \to \operatorname{Zn}^{2+} + 2e^{-}$$

The overall reaction is:

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

Conclusion:

A redox reaction has taken place. Cu^{2+} ions are reduced and the zinc is oxidised.

Below are some further examples of redox reactions:

• $H_2 + F_2 \rightarrow 2 HF$ can be re-written as two half-reactions:

 $H_2 \to 2 H^+ + 2 e^-$ (oxidation) and $F_2 + 2 e^- \to 2 F^- \mbox{ (reduction)}$

• $Cl_2 + 2KI \rightarrow 2KCl + I_2$ or $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$, can be written as two half-reactions:

 $Cl_2 + 2e^- \rightarrow 2Cl^-$ (reduction) and $2I^- \rightarrow I_2 + 2e^-$ (oxidation)

In Grade 12, you will go on to look at electrochemical reactions, and the role that electron transfer plays in this type of reaction.

Exercise: Redox Reactions

1. Look at the following reaction:

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

- (a) What is the oxidation number of the oxygen atom in each of the following compounds?
 - i. H₂O₂
 - ii. H₂O
 - iii. O_2
- (b) Does the hydrogen peroxide (H_2O_2) act as an oxidising agent or a reducing agent or both, in the above reaction? Give a reason for your answer.
- 2. Consider the following chemical equations:
 - 1. Fe(s) \rightarrow Fe²⁺(aq) + 2e⁻

2. $4H^+(aq)+O_2(g)+4e^-\rightarrow 2H_2O(l)$ Which one of the following statements is correct?

- (a) Fe is oxidised and H^+ is reduced
- (b) Fe is reduced and O_2 is oxidised
- (c) Fe is oxidised and O_2 is reduced
- (d) Fe is reduced and H^+ is oxidised

(DoE Grade 11 Paper 2, 2007)

- 3. Which one of the following reactions is a redox reaction?
 - (a) $HCl + NaOH \rightarrow NaCl + H_2O$
 - (b) $AgNO_3 + NaI \rightarrow AgI + NaNO_3$
 - (c) $2\text{FeCl}_3 + 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HCl} + 2\text{FeCl}_2$
 - (d) $BaCl_2 + MgSO_4 \rightarrow MgCl_2 + BaSO_4$

15.3 Addition, substitution and elimination reactions

15.3.1 Addition reactions

An addition reaction occurs when two or more reactants combine to form a final product. This product will contain *all* the atoms that were present in the reactants. The following is a general equation for this type of reaction:

$$A + B \rightarrow C$$

Notice that C is the final product with no A or B remaining as a residue.

The following are some examples.

1. The reaction between ethene and bromine to form 1,2-dibromoethane (figure 15.1).

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$



Figure 15.1: The reaction between ethene and bromine is an example of an addition reaction

2. Polymerisation reactions

In industry, making polymers is very important. A polymer is made up of lots of smaller units called *monomers*. When these monomers are added together, they form a polymer. Examples of polymers are polyvinylchloride (PVC) and polystyrene. PVC is often used to make piping, while polystyrene is an important packaging and insulating material. Polystyrene is made up of lots of styrene monomers which are joined through addition reactions (figure 15.2). 'Polymerisation' refers to the addition reactions that eventually help to form the polystyrene polymer.



Figure 15.2: The polymerisation of a styrene monomer to form a polystyrene polymer

3. The **hydrogenation** of vegetable oils to form margarine is another example of an addition reaction. Hydrogenation involves adding hydrogen (H_2) to an alkene. An alkene is an organic compound composed of carbon and hydrogen. It contains a double bond between two of the carbon atoms. If this bond is broken, it means that more hydrogen atoms can attach themselves to the carbon atoms. During hydrogenation, this double bond is broken, and more hydrogen atoms are added to the molecule. The reaction that takes place is shown below. Note that the 'R' represents any side-chain. A side-chain is simply any combination of atoms that are attached to the central part of the molecule.

$$RCHCH_2 + H_2 \rightarrow RCH_2CH_3$$

4. The production of the alcohol ethanol from ethene. Ethanol (CH_3CH_2OH) can be made from alkenes such as ethene (C_2H_4), through a hydration reaction like the one below. A hydration reaction is one where water is added to the reactants.

$$C_2H_4 + H_2O \rightarrow CH_3CH_2OH$$

A catalyst is needed for this reaction to take place. The catalyst that is most commonly used is phosphoric acid.

15.3.2 Elimination reactions

An elimination reaction occurs when a reactant is broken up into two products. The general form of the equation is as follows:

$$A \rightarrow B + C$$

The examples below will help to explain this:

1. The **dehydration of an alcohol** is one example. Two hydrogen atoms and one oxygen atom are eliminated and a molecule of water is formed as a second product in the reaction, along with an alkene.

$$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$$



2. The elimination of potassium bromide from a bromoalkane.

$$\rm CH_3CH_2Br + \rm KOH \rightarrow \rm CH_2CH_2 + \rm KBr + \rm H_2O$$

$$\begin{array}{ccccccc} H & Br & H & H \\ | & | & | & | \\ H - C & - C & - H + & KOH \longrightarrow & C = C & + & KBr & + & H_2O \\ | & | & | & | & | \\ H & H & H & H & H \end{array}$$

3. Ethane cracking is an important industrial process used by SASOL and other petrochemical industries. Hydrogen is eliminated from ethane (C_2H_6) to produce an alkene called ethene (C_2H_4) . Ethene is then used to produce other products such as polyethylene. You will learn more about these compounds in chapter 23. The equation for the cracking of ethane looks like this:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

15.3.3 Substitution reactions

A substitution reaction occurs when an exchange of reactants takes place. The initial reactants are transformed or 'swopped around' to give a final product. A simple example of a reaction like this is shown below:

$$AB + CD \rightarrow AC + BD$$

Some simple examples of substitution reactions are shown below:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

In this example, a chorine atom and a hydrogen atom are exchanged to create a new product.

$$Cu(H_2O)_4^{2+} + 4Cl^- \Leftrightarrow Cu(Cl)_4^{2-} + 4H_2O$$

Exercise: Addition, substitution and elimination reactions

1. Refer to the diagram below and then answer the questions that follow:

$$\begin{array}{cccccccc} H & CI & H & H \\ I & I & I \\ H - C & C & H + KOH \longrightarrow & C = C + KCI + H_2O \\ I & I & I \\ (i) & H & H & H \end{array}$$

- (a) Is this reaction an example of substitution, elimination or addition?
- (b) Give a reason for your answer above.
- (c) What type of compound is the reactant marked (i)?
- 2. The following diagram shows the reactants in an addition reaction.
 - $\begin{array}{ccc} H & H \\ I & I \\ C = C + HCI & ---- \\ I & I \\ H & H \end{array}$
 - (a) Draw the final product in this reaction.
 - (b) What is the chemical formula of the product?
- 3. The following reaction takes place:

$$\begin{array}{ccccccccccccc} H & OH & H & H & H \\ I & I & I & I & I & I \\ H & C & -C & -H & \frac{H_2SO_4}{2} & C & =C & +H_2O \\ I & I & I & I & I \\ H & H & H & H & H \end{array}$$

Is this reaction a substitution, addition or dehydration reaction? Give a reason for your answer.

4. Consider the following reaction:

 $Ca(OH)_2(s) + 2NH_4Cl(s) \rightarrow CaCl_2(s) + 2NH_3(g) + 2H_2O(g)$

Which one of the following best describes the type of reaction which takes place?

- (a) Redox reaction
- (b) Acid-base reaction
- (c) Dehydration reaction

15.4 Summary

- There are many different **types of reactions** that can take place. These include acid-base, acid-carbonate, redox, addition, substitution and elimination reactions.
- The Arrhenius definition of acids and bases defines an acid as a substance that increases the concentration of hydrogen ions (H⁺ or H₃O⁺) in a solution. A base is a substance that increases the concentration of hydroxide ions (OH⁻) in a solution. However this definition only applies to substances that are in water.
- The Bronsted-Lowry definition is a much broader one. An acid is a substance that donates protons and a base is a substance that accepts protons.
- In different reactions, certain substances can act as both an acid and a base. These
 substances are called **ampholytes** and are said to be **amphoteric**. Water is an example
 of an amphoteric substance.
- A conjugate acid-base pair refers to two compounds in a reaction that change into other through the loss or gain of a proton.
- When an acid and a base react, they form a salt and water. The salt is made up of a cation from the base and an anion from the acid. An example of a salt is sodium chloride (NaCl), which is the product of the reaction between sodium hydroxide (NaOH) and hydrochloric acid (HCl).
- The reaction between an acid and a base is a neutralisation reaction.
- **Titrations** are reactions between an acid and a base that are used to calculate the concentration of one of the reacting substances. The concentration of the other reacting substance must be known.
- In an **acid-carbonate reaction**, an acid and a carbonate react to form a salt, carbon dioxide and water.
- A redox reaction is one where there is always a change in the oxidation numbers of the elements that are involved in the reaction.
- Oxidation is the loss of electrons and reduction is the gain of electrons.

- When two or more reactants combine to form a product that contains all the atoms that were in the reactants, then this is an **addition reaction**. Examples of addition reactions include the reaction between ethene and bromine, polymerisation reactions and hydrogenation reactions.
- A reaction where the reactant is broken down into one or more product, is called an elimination reaction. Alcohol dehydration and ethane cracking are examples of elimination reactions.
- A substitution reaction is one where the reactants are transformed or swopped around to form the final product.

15.4

Exercise: Summary Exercise

- 1. Give one word/term for each of the following descriptions:
 - (a) A chemical reaction during which electrons are transferred
 - (b) The addition of hydrogen across a double bond
 - (c) The removal of hydrogen and halogen atoms from an alkane to form an elkene
- 2. For each of the following, say whether the statement is true or false. If the statement is false, re-write the statement correctly.
 - (a) The conjugate base of NH_4^+ is NH_3 .
 - (b) The reactions $C+O_2\to CO_2$ and $2KClO_3\to 2KCl+3O_2$ are examples of redox reactions.
- 3. For each of the following questions, choose the one correct statement from the list provided.
 - A The following chemical equation represents the formation of the hydronium ion:

$$H^+(aq) + H_2O(l) \rightarrow H_3O^+(aq)$$

In this reaction, water acts as a Lewis base because it...

- i. accepts protons
- ii. donates protons
- iii. accepts electrons
- iv. donates electrons
- B What is the concentration (in mol.dm⁻³) of H₃O⁺ ions in a NaOH solution which has a pH of 12 at 25⁰C?
 - i. $1\,\times\,10^{12}$
 - ii. 1×10^2
 - iii. 1×10^{-2}
 - iv. 1×10^{-12}
 - (IEB Paper 2, 2005)
- C When chlorine water is added to a solution of potassium bromide, bromine is produced. Which one of the following statements concerning this reaction is correct?
 - i. Br^- is oxidised
 - ii. Cl₂ is oxidised
 - iii. Br^- is the oxidising agent
 - iv. CI^- is the oxidising agent

(IEB Paper 2, 2005)

4. The stomach secretes gastric juice, which contains hydrochloric acid. The gastric juice helps with digestion. Sometimes there is an overproduction of acid, leading to heartburn or indigestion. Antacids, such as milk of magnesia, can be taken to neutralise the excess acid. Milk of magnesia is only slightly soluble in water and has the chemical formula Mg(OH)₂.

- a Write a balanced chemical equation to show how the antacid reacts with the acid.
- b The directions on the bottle recommend that children under the age of 12 years take one teaspoon of milk of magnesia, whereas adults can take two teaspoons of the antacid. Briefly explain why the dosages are different.
- c Why is it not advisable to take an overdose of the antacid in the stomach? Refer to the hydrochloric acid concentration in the stomach in your answer. In an experiment, 25.0 cm³ of a standard solution of sodium carbonate of concentration 0.1 mol.dm⁻³ was used to neutralise 35.0 cm³ of a solution of hydrochloric acid.
- d Write a balanced chemical equation for the reaction.
- $\ensuremath{\mathsf{e}}$ Calculate the concentration of the acid.

(DoE Grade 11 Exemplar, 2007)

Chapter 16

Reaction Rates - Grade 12

16.1 Introduction

Before we begin this section, it might be useful to think about some different types of reactions and how quickly or slowly they occur.



Exercise: Thinking about reaction rates

Think about each of the following reactions:

- rusting of metals
- photosynthesis
- weathering of rocks (e.g. limestone rocks being weathered by water)
- combustion
- 1. For each of the reactions above, write a chemical equation for the reaction that takes place.
- 2. How fast is each of these reactions? Rank them in order from the fastest to the slowest.
- 3. How did you decide which reaction was the fastest and which was the slowest?
- 4. Try to think of some other examples of chemical reactions. How fast or slow is each of these reactions, compared with those listed earlier?

In a chemical reaction, the substances that are undergoing the reaction are called the **reactants**, while the substances that form as a result of the reaction are called the **products**. The **reaction rate** describes how quickly or slowly the reaction takes place. So how do we know whether a reaction is slow or fast? One way of knowing is to look either at how quickly the *reactants are used up* during the reaction or at how quickly the *product forms*. For example, iron and sulfur react according to the following equation:

$$Fe+S \to FeS$$

In this reaction, we can see the speed of the reaction by observing how long it takes before there is no iron or sulfur left in the reaction vessel. In other words, the reactants have been used up. Alternatively, one could see how quickly the iron sulfide product forms. Since iron sulfide looks very different from either of its reactants, this is easy to do.

In another example:

 $2Mg(s) + O_2 \rightarrow 2MgO(s)$

In this case, the reaction rate depends on the speed at which the reactants (solid magnesium and oxygen gas) are used up, or the speed at which the product (magnesium oxide) is formed.

Definition: Reaction rate

The rate of a reaction describes how quickly reactants are used up or how quickly products are formed during a chemical reaction. The units used are: moles per second (mols/second or mol.s⁻¹).

The average rate of a reaction is expressed as the number of moles of reactant used up, divided by the total reaction time, or as the number of moles of product formed, divided by the reaction time. Using the magnesium reaction shown earlier:

Average reaction rate =
$$\frac{moles \ Mg \ used}{reaction \ time \ (s)}$$

or

Average reaction rate =
$$\frac{moles O_2 used}{reaction time (s)}$$

or

Average reaction rate = $\frac{moles \ MgO \ produced}{reaction \ time \ (s)}$

Worked Example 76: Reaction rates

Question: The following reaction takes place:

$$4Li + O_2 \rightarrow 2Li_2O$$

After two minutes , 4 g of Lithium has been used up. Calculate the rate of the reaction.

Answer

Step 1 : Calculate the number of moles of Lithium that are used up in the reaction.

$$n = \frac{m}{M} = \frac{4}{6.94} = 0.58mols$$

Step 2 : Calculate the time (in seconds) for the reaction.

$$t = 2 \times 60 = 120s$$

Step 3 : Calculate the rate of the reaction. Rate of reaction =

$$\frac{moles \ of \ Lithium \ used}{time} = \frac{0.58}{120} = 0.005$$

The rate of the reaction is 0.005 $\rm mol.s^{-1}$



Exercise: Reaction rates

1. A number of different reactions take place. The table below shows the number of moles of reactant that are used up in a particular time for each reaction.

Reaction	Mols used up	Time	Reaction rate
1	2	30 secs	
2	5	2 mins	
3	1	1.5 mins	
4	3.2	1.5 mins	
5	5.9	30 secs	

- (a) Complete the table by calculating the rate of each reaction.
- (b) Which is the *fastest* reaction?
- (c) Which is the *slowest* reaction?
- 2. Two reactions occur simultaneously in separate reaction vessels. The reactions are as follows:

$$Mg + Cl_2 \rightarrow MgCl_2$$
$$2Na + Cl_2 \rightarrow 2NaCl_2$$

After 1 minute, 2 g of $MgCl_2$ have been produced in the first reaction.

- (a) How many moles of $MgCl_2$ are produced after 1 minute?
- (b) Calculate the rate of the reaction, using the amount of product that is produced.
- (c) Assuming that the second reaction also proceeds at the same rate, calculate...

i. the number of moles of NaCl produced after 1 minute.

ii. the mass (in g) of sodium that is needed for this reaction to take place.

16.2 Factors affecting reaction rates

Several factors affect the rate of a reaction. It is important to know these factors so that reaction rates can be controlled. This is particularly important when it comes to industrial reactions, so that productivity can be maximised. The following are some of the factors that affect the rate of a reaction.

1. Nature of reactants

Substances have different chemical properties and therefore react differently and at different rates.

2. Concentration (or pressure in the case of gases)

As the concentration of the reactants increases, so does the reaction rate.

3. Temperature

If the temperature of the reaction increases, so does the rate of the reaction.

4. Catalyst

Adding a catalyst increases the reaction rate.

5. Surface area of solid reactants

Increasing the surface area of the reactants (e.g. if a solid reactant is finely broken up) will increase the reaction rate.

Activity :: Experiment : The nature of reactants. Aim:

To determine the effect of the nature of reactants on the rate of a reaction. Apparatus:

Oxalic acid ((COOH)₂), iron(II) sulphate (FeSO₄), potassium permanganate (KMnO₄), concentrated sulfuric acid (H₂SO₄), spatula, test tubes, medicine dropper, glass beaker and glass rod.



Method:

- 1. In the first test tube, prepare an iron (II) sulphate solution by dissolving about two spatula points of iron (II) sulphate in 10 cm³ of water.
- 2. In the second test tube, prepare a solution of oxalic acid in the same way.
- 3. Prepare a solution of sulfuric acid by adding 1 cm³ of the concentrated acid to about 4 cm³ of water. Remember always to add the *acid to the water*, and never the other way around.
- 4. Add 2 cm³ of the sulfuric acid solution to the iron(II) and oxalic acid solutions respectively.
- 5. Using the medicine dropper, add a few drops of potassium permanganate to the two test tubes. Once you have done this, observe how quickly each solution discolours the potassium permanganate solution.

Results:

- You should have seen that the oxalic acid solution discolours the potassium permanganate much more slowly than the iron(II) sulphate.
- It is the oxalate ions $(C_2O_4^{2-})$ and the Fe²⁺ ions that cause the discolouration. It is clear that the Fe²⁺ ions act much more quickly than the $C_2O_4^{2-}$ ions. The reason for this is that there are no covalent bonds to be broken in the ions before the reaction can take place. In the case of the oxalate ions, covalent bonds between carbon and oxygen atoms must be broken first.

Conclusions:

The nature of the reactants can affect the rate of a reaction.



Oxalic acids are abundant in many plants. The leaves of the tea plant (*Camellia sinensis*) contain very high concentrations of oxalic acid relative to other plants. Oxalic acid also occurs in small amounts in foods such as parsley, chocolate, nuts and berries. Oxalic acid irritates the lining of the gut when it is eaten, and can be fatal in very large doses.

Activity :: Experiment : Surface area and reaction rates.

Marble $(CaCO_3)$ reacts with hydrochloric acid (HCl) to form calcium chloride, water and carbon dioxide gas according to the following equation:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

Aim:

To determine the effect of the surface area of reactants on the rate of the reaction. **Apparatus:**

2 g marble chips, 2 g powdered marble, hydrochloric acid, beaker, two test tubes.



Method:

- 1. Prepare a solution of hydrochloric acid in the beaker by adding 2 cm³ of the concentrated solution to 20 cm³ of water.
- 2. Place the marble chips and powdered marble into separate test tubes.
- 3. Add 10 cm³ of the dilute hydrochloric acid to each of the test tubes and observe the rate at which carbon dioxide gas is produced.

Results:

- Which reaction proceeds the fastest?
- Can you explain this?

Conclusions:

The reaction with powdered marble is the fastest. The smaller the pieces of marble are, the greater the surface area for the reaction to take place. The greater the surface area of the reactants, the faster the reaction rate will be.

Activity :: Experiment : Reactant concentration and reaction rate. Aim:

To determine the effect of reactant concentration on reaction rate. Apparatus:

Concentrated hydrochloric acid (HCl), magnesium ribbon, two beakers, two test tubes, measuring cylinder. **Method:**

- 1. Prepare a solution of dilute hydrochloric acid in one of the beakers by diluting 1 part concentrated acid with 10 parts water. For example, if you measure 1 cm³ of concentrated acid in a measuring cylinder and pour it into a beaker, you will need to add 10 cm³ of water to the beaker as well. In the same way, if you pour 2 cm³ of concentrated acid into a beaker, you will need to add 20 cm³ of water. Both of these are 1:10 solutions. Pour 10 cm³ of the 1:10 solution into a test tube and mark it 'A'. Remember to add the *acid* to the *water*, and not the other way around.
- Prepare a second solution of dilute hydrochloric acid by diluting 1 part concentrated acid with 20 parts water. Pour 10cm³ of this 1:20 solution into a second test tube and mark it 'B'.
- 3. Take two pieces of magnesium ribbon of the **same length**. At the same time, put one piece of magnesium ribbon into test tube A and the other into test tube B, and observe closely what happens.



The equation for the reaction is:

$$2HCl + Mg \rightarrow MgCl_2 + H_2$$

Results:

- Which of the two solutions is more concentrated, the 1:10 or 1:20 hydrochloric acid solution?
- In which of the test tubes is the reaction the fastest? Suggest a reason for this.
- How can you measure the rate of this reaction?
- What is the gas that is given off?
- Why was it important that the same length of magnesium ribbon was used for each reaction?

Conclusions:

The 1:10 solution is more concentrated and this reaction therefore proceeds faster. The greater the concentration of the reactants, the faster the rate of the reaction. The rate of the reaction can be measured by the rate at which hydrogen gas is produced.

Activity :: Group work : The effect of temperature on reaction rate

- 1. In groups of 4-6, design an experiment that will help you to see the effect of temperature on the reaction time of 2 cm of magnesium ribbon and 20 ml of vinegar. During your group discussion, you should think about the following:
 - What equipment will you need?
 - How will you conduct the experiment to make sure that you are able to compare the results for different temperatures?
 - How will you record your results?
 - What safety precautions will you need to take when you carry out this experiment?
- 2. Present your experiment ideas to the rest of the class, and give them a chance to comment on what you have done.
- 3. Once you have received feedback, carry out the experiment and record your results.
- 4. What can you conclude from your experiment?

16.3 Reaction rates and collision theory

It should be clear now that the rate of a reaction varies depending on a number of factors. But how can we *explain* why reactions take place at different speeds under different conditions? Why, for example, does an increase in the surface area of the reactants also increase the rate of the reaction? One way to explain this is to use **collision theory**.

For a reaction to occur, the particles that are reacting must collide with one another. Only a fraction of all the collisions that take place actually cause a chemical change. These are called 'successful' collisions. When there is an increase in the *concentration* of reactants, the chance that reactant particles will collide with each other also increases because there are more particles in that space. In other words, the *collision frequency* of the reactants increases. The number of *successful* collisions will therefore also increase, and so will the rate of the reaction. In the same way, if the *surface area* of the reactants increases, there is also a greater chance that successful collisions will occur.

Definition: Collision theory

Collision theory is a theory that explains how chemical reactions occur and why reaction rates differ for different reactions. The theory assumes that for a reaction to occur the reactant particles must collide, but that only a certain fraction of the total collisions, the *effective collisions*, actually cause the reactant molecules to change into products. This is because only a small number of the molecules have enough energy and the right orientation at the moment of impact to break the existing bonds and form new bonds.

When the *temperature* of the reaction increases, the average kinetic energy of the reactant particles increases and they will move around much more actively. They are therefore more likely to collide with one another (Figure 16.1). Increasing the temperature also increases the number of particles whose energy will be greater than the activation energy for the reaction (refer section 16.5).



Figure 16.1: An increase in the temperature of a reaction increases the chances that the reactant particles (A and B) will collide because the particles have more energy and move around more.

Exercise: Rates of reaction

Hydrochloric acid and calcium carbonate react according to the following equation:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$$

The volume of carbon dioxide that is produced during the reaction is measured at different times. The results are shown in the table below.

Time (mins)	Volume of CO $_2$ produced (cm 3)
1	14
2	26
3	36
4	44
5	50
6	58
7	65
8	70
9	74
10	77

Note: On a graph of production against time, it is the gradient of the graph that shows the rate of the reaction.

Questions:

- 1. Use the data in the table to draw a graph showing the volume of gas that is produced in the reaction, over a period of 10 minutes.
- 2. At which of the following times is the reaction *fastest*? Time = 1 minute; time = 6 minutes or time = 8 minutes.
- 3. Suggest a reason why the reaction slows down over time.
- 4. Use the graph to estimate the volume of gas that will have been produced after 11 minutes.
- 5. After what time do you think the reaction will stop?
- 6. If the experiment was repeated using a more concentrated hydrochloric acid solution...
 - (a) would the rate of the reaction increase or decrease from the one shown in the graph?
 - (b) draw a rough line on the graph to show how you would expect the reaction to proceed with a more concentrated HCl solution.

16.4 Measuring Rates of Reaction

How the rate of a reaction is measured will depend on what the reaction is, and what product forms. Look back to the reactions that have been discussed so far. In each case, how was the rate of the reaction measured? The following examples will give you some ideas about other ways to measure the rate of a reaction:

• Reactions that produce hydrogen gas:

When a metal dissolves in an acid, hydrogen gas is produced. A lit splint can be used to test for hydrogen. The 'pop' sound shows that hydrogen is present. For example, magnesium reacts with sulfuric acid to produce magnesium sulphate and hydrogen.

$$Mg(s) + H_2SO_4 \rightarrow MgSO_4 + H_2$$

• Reactions that produce carbon dioxide:

When a carbonate dissolves in an acid, carbon dioxide gas is produced. When carbon dioxide is passes through limewater, it turns the limewater milky. This is the test for the presence of carbon dioxide. For example, calcium carbonate reacts with hydrochloric acid to produce calcium chloride, water and carbon dioxide.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(q)$$

• Reactions that produce gases such as oxygen or carbon dioxide:

Hydrogen peroxide decomposes to produce oxygen. The volume of oxygen produced can be measured using the gas syringe method (figure 16.2). The gas collects in the syringe, pushing out against the plunger. The volume of gas that has been produced can be read from the markings on the syringe. For example, hydrogen peroxide decomposes in the presence of a manganese(IV) oxide catalyst to produce oxygen and water.

$$2H_2O_2(aq) \to 2H_2O(l) + O_2(g)$$



Reactants

Figure 16.2: Gas Syringe Method

• Precipitate reactions:

In reactions where a *precipitate* is formed, the amount of precipitate formed in a period of time can be used as a measure of the reaction rate. For example, when sodium thiosulphate reacts with an acid, a yellow precipitate of sulfur is formed. The reaction is as follows:

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(aq) + H_2O(l) + S(s)$$
295

One way to estimate the rate of this reaction is to carry out the investigation in a conical flask and to place a piece of paper with a black cross underneath the bottom of the flask. At the beginning of the reaction, the cross will be clearly visible when you look into the flask (figure 16.3). However, as the reaction progresses and more precipitate is formed, the cross will gradually become less clear and will eventually disappear altogether. Noting the time that it takes for this to happen will give an idea of the reaction rate. Note that it is not possible to collect the SO_2 gas that is produced in the reaction, because it is very soluble in water.

[glassType=erlen,niveauLiquide1=40]



Figure 16.3: At the beginning of the reaction beteen sodium thiosulphate and hydrochloric acid, when no precipitate has been formed, the cross at the bottom of the conical flask can be clearly seen.

• Changes in mass:

The rate of a reaction that produces a gas can also be measured by calculating the mass loss as the gas is formed and escapes from the reaction flask. This method can be used for reactions that produce carbon dioxide or oxygen, but are not very accurate for reactions that give off hydrogen because the mass is too low for accuracy. Measuring changes in mass may also be suitable for other types of reactions.

Activity :: Experiment : Measuring reaction rates Aim:

To measure the effect of concentration on the rate of a reaction. **Apparatus:**

- 300 cm³ of sodium thiosulphate (Na₂S₂O₃) solution. Prepare a solution of sodium thiosulphate by adding 12 g of Na₂S₂O₃ to 300 cm³ of water. This is solution 'A'.
- 300 cm³ of water
- 100 cm 3 of 1:10 dilute hydrochloric acid. This is solution 'B'.
- Six 100 cm³ glass beakers
- Measuring cylinders
- Paper and marking pen
- Stopwatch or timer

Method:

One way to measure the rate of this reaction is to place a piece of paper with a cross underneath the reaction beaker to see how quickly the cross is made invisible by the formation of the sulfur precipitate.

- 1. Set up six beakers on a flat surface and mark them from 1 to 6. Under each beaker you will need to place a piece of paper with a large black cross.
- 2. Pour 60 cm³ solution A into the first beaker and add 20 cm³ of water
- 3. Use the measuring cylinder to measure 10 cm³ HCl. Now add this HCl to the solution that is already in the first beaker (NB: Make sure that you always clean out the measuring cylinder you have used before using it for another chemical).
- 4. Using a stopwatch with seconds, record the time it takes for the precipitate that forms to block out the cross.
- Now measure 50 cm³ of solution A into the second beaker and add 30 cm³ of water. To this second beaker, add 10 cm³ HCl, time the reaction and record the results as you did before.
- Beaker Solution Water (cm³) В Time Α Solution (cm³) (cm³) (s) 60 20 10 1 2 30 10 50 3 40 40 10 4 30 50 10 5 20 60 10 6 10 70 10
- 6. Continue the experiment by diluting solution A as shown below.

The equation for the reaction between sodium thiosulphate and hydrochloric acid is:

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(aq) + H_2O(l) + S(s)$$

Results:

• Calculate the reaction rate in each beaker. This can be done using the following equation:

Rate of reaction
$$= \frac{1}{time}$$

- Represent your results on a graph. Concentration will be on the x-axis and reaction rate on the y-axis. Note that the original volume of Na₂S₂O₃ can be used as a measure of concentration.
- Why was it important to keep the volume of HCl constant?
- Describe the relationship between concentration and reaction rate.

Conclusions:

The rate of the reaction is fastest when the concentration of the reactants was the highest.

16.5 Mechanism of reaction and catalysis

Earlier it was mentioned that it is the *collision* of particles that causes reactions to occur and that only some of these collisions are 'successful'. This is because the reactant particles have a wide range of kinetic energy, and only a small fraction of the particles will have enough energy to actually break bonds so that a chemical reaction can take place. The minimum energy that is needed for a reaction to take place is called the **activation energy**. For more information on the energy of reactions, refer to chapter 14.

16.5

Definition: Activation energy

The energy that is needed to break the bonds in reactant molecules so that a chemical reaction can proceed.

Even at a fixed temperature, the energy of the particles varies, meaning that only some of them will have enough energy to be part of the chemical reaction, depending on the activation energy for that reaction. This is shown in figure 16.4. Increasing the reaction temperature has the effect of increasing the number of particles with enough energy to take part in the reaction, and so the reaction rate increases.



Figure 16.4: The distribution of particle kinetic energies at a fixed temperature

A **catalyst** functions slightly differently. The function of a catalyst is to lower the activation energy so that more particles now have enough energy to react. The catalyst itself is not changed during the reaction, but simply provides an alternative pathway for the reaction, so that it needs less energy. Some *metals* e.g. platinum, copper and iron can act as catalysts in certain reactions. In our own human bodies, *enzymes* are catalysts that help to speed up biological reactions. Catalysts generally react with one or more of the reactants to form a chemical intermediate which then reacts to form the final product. The chemical intermediate is sometimes called the **activated complex**.

The following is an example of how a reaction that involves a catalyst might proceed. C represents the catalyst, A and B are reactants and D is the product of the reaction of A and B.

In the above, ABC represents the intermediate chemical. Although the catalyst (C) is consumed by reaction 1, it is later produced again by reaction 4, so that the overall reaction is as follows:

$$A + B + C \rightarrow D + C$$

You can see from this that the catalyst is released at the end of the reaction, completely unchanged.



Definition: Catalyst

A catalyst speeds up a chemical reaction, without being altered in any way. It increases the reaction rate by lowering the activation energy for a reaction.

Energy diagrams are useful to illustrate the effect of a **catalyst** on reaction rates. Catalysts decrease the activation energy required for a reaction to proceed (shown by the smaller 'hump' on the energy diagram in figure 16.5), and therefore increase the reaction rate.



Figure 16.5: The effect of a catalyst on the activation energy of a reaction

Activity :: Experiment : Catalysts and reaction rates Aim:

To determine the effect of a catalyst on the rate of a reaction **Apparatus:**

Zinc granules, 0.1 M hydrochloric acid, copper pieces, one test tube and a glass beaker.

Method:

- 1. Place a few of the zinc granules in the test tube.
- 2. Measure the mass of a few pieces of copper and keep them separate from the rest of the copper.
- Add about 20 cm³ of HCl to the test tube. You will see that a gas is released. Take note of how quickly or slowly this gas is released. Write a balanced equation for the chemical reaction that takes place.
- 4. Now add the copper pieces to the same test tube. What happens to the rate at which the gas is produced?
- 5. Carefully remove the copper pieces from the test tube (do not get HCl on your hands), rinse them in water and alcohol and then weigh them again. Has the mass of the copper changed since the start of the experiment?

Results:

During the reaction, the gas that is released is hydrogen. The rate at which the hydrogen is produced *increases* when the copper pieces (the catalyst) are added. The mass of the copper does not change during the reaction. **Conclusions:**

The copper acts as a *catalyst* during the reaction. It speeds up the rate of the reaction, but is not changed in any way itself.

Exercise: Reaction rates

- 1. For each of the following, say whether the statement is **true** or **false**. If it is false, re-write the statement correctly.
 - (a) A catalyst increases the energy of reactant molecules so that a chemical reaction can take place.
 - (b) Increasing the temperature of a reaction has the effect of increasing the number of reactant particles that have more energy that the activation energy.
 - (c) A catalyst does not become part of the final product in a chemical reaction.
- 2. 5 g of zinc granules are added to 400 cm³ of 0.5 mol.dm⁻³ hydrochloric acid. To investigate the rate of the reaction, the change in the mass of the flask containing the zinc and the acid was measured by placing the flask on a direct reading balance. The reading on the balance shows that there is a decrease in mass during the reaction. The reaction which takes place is given by the following equation:

 $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

- (a) Why is there a decrease in mass during the reaction?
- (b) The experiment is repeated, this time using 5 g of powdered zinc instead of granulated zinc. How will this influence the rate of the reaction?
- (c) The experiment is repeated once more, this time using 5 g of granulated zinc and 600 cm³ of 0.5 mol.dm⁻³ hydrochloric acid. How does the rate of this reaction compare to the **original** reaction rate?
- (d) What effect would a catalyst have on the rate of this reaction?
- (IEB Paper 2 2003)
- 3. Enzymes are catalysts. Conduct your own research to find the names of common enzymes in the human body and which chemical reactions they play a role in.
- 4. 5 g of calcium carbonate powder reacts with 20 cm³ of a 0.1 mol.dm⁻³ solution of hydrochloric acid. The gas that is produced at a temperature of 25⁰C is collected in a gas syringe.
 - (a) Write a balanced chemical equation for this reaction.
 - (b) The rate of the reaction is determined by measuring the volume of gas thas is produced in the first minute of the reaction. How would the rate of the reaction be affected if:
 - i. a lump of calcium carbonate of the same mass is used
 - ii. 40 cm³ of 0.1 mol.dm⁻³ hydrochloric acid is used

16.6 Chemical equilibrium

Having looked at factors that affect the rate of a reaction, we now need to ask some important questions. Does a reaction always proceed in the same direction or can it be reversible? In other words, is it always true that a reaction proceeds from *reactants to products*, or is it possible that sometimes, the reaction will reverse and the *products will be changed back into the reactants*? And does a reaction always run its full course so that all the reactants are used up, or can a reaction reach a point where reactants are still present, but there does not seem to be any further change taking place in the reaction? The following demonstration might help to explain this.

Activity :: Demonstration : Liquid-vapour phase equilibrium Apparatus and materials: 2 beakers; water; bell jar Method:

- 1. Half fill two beakers with water and mark the level of the water in each case.
- 2. Cover one of the beakers with a bell jar.
- 3. Leave the beakers and, over the course of a day or two, observe how the water level in the two beakers changes. What do you notice? Note: You could speed up this demonstration by placing the two beakers over a bunsen burner to heat the water. In this case, it may be easier to cover the second beaker with a glass cover.

Observations:

You should notice that in the beaker that is uncovered, the water level drops quickly because of evaporation. In the beaker that is covered, there is an initial drop in the water level, but after a while evaporation appears to stop and the water level in this beaker is higher than that in the one that is open. Note that the diagram below shows the situation ate time=0.



Discussion:

In the first beaker, liquid water becomes water vapour as a result of evaporation and the water level drops. In the second beaker, evaporation also takes place. However, in this case, the vapour comes into contact with the surface of the bell jar and it cools and condenses to form liquid water again. This water is returned to the beaker. Once condensation has begun, the rate at which water is lost from the beaker will start to decrease. At some point, the rate of evaporation will be equal to the rate of condensation above the beaker, and there will be no change in the water level in the beaker. This can be represented as follows:

$liquid \Leftrightarrow vapour$

In this example, the reaction (in this case, a change in the phase of water) can proceed in either direction. In one direction there is a change in phase from liquid to vapour. But the reverse can also take place, when vapour condenses to form water again.

In a **closed system** it is possible for reactions to be reversible, such as in the demonstration above. In a closed system, it is also possible for a chemical reaction to reach **equilibrium**. We will discuss these concepts in more detail.

16.6.1 Open and closed systems

An **open system** is one in which matter or energy can flow into or out of the system. In the liquid-vapour demonstration we used, the first beaker was an example of an open system because the beaker could be heated or cooled (a change in *energy*), and water vapour (the *matter*) could evaporate from the beaker.

A **closed system** is one in which energy can enter or leave, but matter cannot. The second beaker covered by the bell jar is an example of a closed system. The beaker can still be heated or cooled, but water vapour cannot leave the system because the bell jar is a barrier. Condensation changes the vapour to liquid and returns it to the beaker. In other words, there is no loss of matter from the system.



Definition: Open and closed systems

An *open system* is one whose borders allow the movement of energy and matter into and out of the system. A *closed system* is one in which only energy can be exchanged, but not matter.

16.6.2 Reversible reactions

Some reactions can take place in two directions. In one direction the reactants combine to form the products. This is called the **forward reaction**. In the other, the products react to form reactants again. This is called the **reverse reaction**. A special double-headed arrow is used to show this type of **reversible reaction**:

$$XY + Z \Leftrightarrow X + YZ$$

So, in the following reversible reaction:

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

The forward reaction is $H_2(g) + I_2(g) \rightarrow 2HI(g)$. The reverse reaction is $2HI(g) \rightarrow H_2(g) + I_2(g)$.



Definition: A reversible reaction

A reversible reaction is a chemical reaction that can proceed in both the forward and reverse directions. In other words, the reactant and product of one reaction may reverse roles.

Activity :: Demonstration : The reversibility of chemical reactions Apparatus and materials:

Lime water $(Ca(OH)_2)$; calcium carbonate $(CaCO_3)$; hydrochloric acid; 2 test tubes with rubber stoppers; delivery tube; retort stand and clamp; bunsen burner. **Method and observations:**

- 1. Half-fill a test tube with clear lime water $(Ca(OH)_2)$.
- 2. In another test tube, place a few pieces of calcium carbonate $(CaCO_3)$ and cover the pieces with dilute hydrochloric acid. Seal the test tube with a rubber stopper and delivery tube.
- 3. Place the other end of the delivery tube into the test tube containing the lime water so that the carbon dioxide that is produced from the reaction between calcium carbonate and hydrochloric acid passes through the lime water. Observe what happens to the appearance of the lime water.

The equation for the reaction that takes place is:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

 $CaCO_3$ is insoluble and it turns the limewater milky.

4. Allow the reaction to proceed for a while so that carbon dioxide continues to pass through the limewater. What do you notice? The equation for the reaction that takes place is:

$$CaCO_3(s) + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

In this reaction, calcium carbonate becomes one of the reactants to produce hydrogen carbonate $(Ca(HCO_3)_2)$ and so the solution becomes clear again.

5. Heat the solution in the test tube over a bunsen burner. What do you observe? You should see bubbles of carbon dioxide appear and the limewater turns milky again. The reaction that has taken place is:



Discussion:

• If you look at the last two equations you will see that the one is the reverse of the other. In other words, this is a *reversible reaction* and can be written as follows:

$$CaCO_3(s) + H_2O + CO_2 \Leftrightarrow Ca(HCO_3)_2$$

• Is the forward reaction endothermic or exothermic? Is the reverse reaction endothermic or exothermic? You should have noticed that the reverse reaction only took place when the solution was heated. Sometimes, changing the temperature of a reaction can change its direction.

16.6.3 Chemical equilibrium

Using the same reversible reaction that we used in an earlier example:

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

The forward reaction is:

 $\begin{array}{c} H_2+I_2 \rightarrow 2HI \\ 303 \end{array}$

The reverse reaction is:

$$2HI \rightarrow H_2 + I_2$$

When the rate of the forward reaction and the reverse reaction are equal, the system is said to be in **equilbrium**. Figure 16.6 shows this. Initially (time = 0), the rate of the forward reaction is high and the rate of the reverse reaction is low. As the reaction proceeds, the rate of the forward reaction decreases and the rate of the reverse reaction increases, until both occur at the same rate. This is called equilibrium.

Although it is not always possible to observe any macroscopic changes, this does not mean that the reaction has stopped. The forward and reverse reactions continue to take place and so microscopic changes still occur in the system. This state is called **dynamic equilibrium**. In the liquid-vapour phase equilibrium demonstration, dynamic equilibrium was reached when there was no observable change in the level of the water in the second beaker even though evaporation and condensation continued to take place.



Figure 16.6: The change in rate of forward and reverse reactions in a closed system

There are, however, a number of factors that can change the chemical equilibrium of a reaction. Changing the **concentration**, the **temperature** or the **pressure** of a reaction can affect equilibrium. These factors will be discussed in more detail later in this chapter.



Definition: Chemical equilibrium

Chemical equilibrium is the state of a chemical reaction, where the concentrations of the reactants and products have no net change over time. Usually, this state results when the forward chemical reactions proceed at the same rate as their reverse reactions.

16.7 The equilibrium constant



Definition: Equilibrium constant

The equilibrium constant (K_c), relates to a chemical reaction at equilibrium. It can be calculated if the equilibrium concentration of each reactant and product in a reaction at equilibrium is known.

16.7.1 Calculating the equilibrium constant

Consider the following generalised reaction which takes place in a **closed** container at a **constant temperature**:

$$A + B \Leftrightarrow C + D$$

We know from section 16.2 that the rate of the forward reaction is directly proportional to the concentration of the reactants. In other words, as the concentration of the reactants increases, so does the rate of the forward reaction. This can be shown using the following equation:

Rate of forward reaction \propto [A][B]

or

Rate of forward reaction = $k_1[A][B]$

Similarly, the rate of the reverse reaction is directly proportional to the concentration of the products. This can be shown using the following equation:

Rate of reverse reaction
$$\propto$$
 [C][D] or
$$\mbox{Rate of reverse reaction} = \mbox{k}_2[\mbox{C}][\mbox{D}]$$

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This can be shown using the following equation:

$$k_1[A][B] = k_2[C][D]$$

or

$$\frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

or, if the constants k_1 and k_2 are simplified to a single constant, the equation becomes:

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

A more general form of the equation for a reaction at chemical equilibrium is:

$$aA + bB \Leftrightarrow cC + dD$$

where A and B are reactants, C and D are products and a, b, c, and d are the coefficients of the respective reactants and products. A more general formula for calculating the equilibrium constant is therefore:

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

It is important to note that if a reactant or a product in a chemical reaction is in either the **liquid** or **solid** phase, the concentration stays constant during the reaction. Therefore, these values can be left out of the equation to calculate k_c . For example, in the following reaction:

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g)$$

305

$$k_c = \frac{[CO][H_2]}{[H_2O]}$$

Important:

- 1. The constant k_c is affected by temperature and so, if the values of k^c are being compared for different reactions, it is important that all the reactions have taken place at the same temperature.
- 2. k_c values do not have units. If you look at the equation, the units all cancel each other out.

16.7.2 The meaning of k_c values

The formula for k_c has the concentration of the products in the numerator and the concentration of reactants in the denominator. So a *high* k_c value means that the concentration of products is high and the reaction has a high yield. We can also say that the equilibrium lies far to the right. The opposite is true for a low k_c value. A *low* k_c value means that, at equilibrium, there are more reactants than products and therefore the yield is low. The equilibrium for the reaction lies far to the left.



Important: Calculations made easy

When you are busy with calculations that involve the equilibrium constant, the following tips may help:

- 1. Make sure that you always read the question carefully to be sure of what you are being asked to calculate. If the equilibrium constant is involved, make sure that the concentrations you use are the concentrations **at equilibrium**, and not the concentrations or quantities that are present at some other time in the reaction.
- 2. When you are doing more complicated calculations, it sometimes helps to draw up a table like the one below and fill in the **mole values** that you know or those you can calculate. This will give you a clear picture of what is happening in the reaction and will make sure that you use the right values in your calculations.

	Reactant 1	Reactant 2	Product 1
Start of reaction			
Used up			
Produced			
Equilibrium			



Worked Example 77: Calculating k_c

Question: For the reaction:

$$SO_2(g) + NO_2(g) \rightarrow NO(g) + SO_3(g)$$

306

the concentration of the reagents is as follows:
$$\label{eq:solution} \begin{split} [SO_3] &= 0.2 \mbox{ mol.dm}^{-3} \\ [NO_2] &= 0.1 \mbox{ mol.dm}^{-3} \\ [NO] &= 0.4 \mbox{ mol.dm}^{-3} \\ [SO_2] &= 0.2 \mbox{ mol.dm}^{-3} \end{split}$$

Calculate the value of k_c .

Answer

Step 1 : Write the equation for \mathbf{k}_c

$$k_c = \frac{[NO][SO_3]}{[SO_2][NO_2]}$$

Step 2 : Fill in the values you know for this equation and calculate k_c

$$k_c = \frac{(0.4 \times 0.2)}{(0.2 \times 0.1)} = 4$$



Worked Example 78: Calculating reagent concentration

Question: For the reaction:

$$S(s) + O_2(g) \Leftrightarrow SO_2(g)$$

- 1. Write an equation for the equilibrium constant.
- 2. Calculate the equilibrium concentration of O_2 if Kc=6 and $[SO_2] = 3mol.dm^{-3}$ at equilibrium.

Answer

Step 1 : Write the equation for k_c

$$k_c = \frac{[SO_2]}{[O_2]}$$

(Sulfur is left out of the equation because it is a solid and its concentration stays constant during the reaction)

Step 2 : Re-arrange the equation so that oxygen is on its own on one side of the equation

$$[O_2] = \frac{[SO_2]}{k_c}$$

Step 3 : Fill in the values you know and calculate [O₂]

$$[O_2] = \frac{3mol.dm^{-3}}{6} = 0.5mol.dm^{-3}$$



Worked Example 79: Equilibrium calculations

Question: Initially 1.4 moles of $NH_3(g)$ is introduced into a sealed 2.0 dm⁻³ reaction vessel. The ammonia decomposes when the temperature is increased to 600K and reaches equilibrium as follows:

 $2NH_3(g) \Leftrightarrow N_2(g) + 3H_2(g)$

When the equilibrium mixture is analysed, the concentration of $NH_3(g)$ is 0.3 mol.dm⁻³

- 1. Calculate the concentration of $N_2(g)$ and $H_2(g)$ in the equilibrium mixture.
- 2. Calculate the equilibrium constant for the reaction at 900 K.

Answer

Step 1 : Calculate the number of moles of NH_3 at equilibrium.

$$c = \frac{n}{V}$$

Therefore,

$$n = c \times V = 0.3 \times 2 = 0.6 mol$$

Step 2 : Calculate the number of moles of ammonia that react (are 'used up') in the reaction.

Moles used up = 1.4 - 0.6 = 0.8 moles

Step 3 : Calculate the number of moles of product that are formed.

Remember to use the mole ratio of reactants to products to do this. In this case, the ratio of $NH_3:N_2:H_2 = 2:1:3$. Therefore, if 0.8 moles of ammonia are used up in the reaction, then 0.4 moles of nitrogen are produced and 1.2 moles of hydrogen are produced.

Step 4 : Complete the following table

	\mathbf{NH}_3	N_2	H_2
Start of reaction	1.4	0	0
Used up	0.8	0	0
Produced	0	0.4	1.2
Equilibrium	0.6	0.4	1.2

Step 5 : Using the values in the table, calculate $[N_2]$ and $[H_2]$

$$[N_2] = \frac{n}{V} = \frac{0.4}{2} = 0.2 \ mol.dm^{-3}$$
$$[H_2] = \frac{n}{V} = \frac{1.2}{2} = 0.6 \ mol.dm^{-3}$$

Step 6 : Calculate k_c

$$k_c = \frac{[H_2]^3[N_2]}{[NH_3]^2} = \frac{(0.6)^3(0.2)}{(0.3)^2} = 0.48$$



Worked Example 80: Calculating k_c

Question: Hydrogen and iodine gas react according to the following equation:

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

When 0.496 mol H_2 and 0.181 mol I_2 are heated at 450° C in a 1 dm³ container, the equilibrium mixture is found to contain 0.00749 mol I_2 . Calculate the equilibrium constant for the reaction at 450° C.

Answer

Step 1 : Calculate the number of moles of iodine used in the reaction. Moles of iodine used = 0.181 - 0.00749 = 0.1735 mol

Step 2 : Calculate the number of moles of hydrogen that are used up in the reaction.

The mole ratio of hydrogen:iodine = 1:1, therefore 0.1735 moles of hydrogen must also be used up in the reaction.

Step 3 : Calculate the number of moles of hydrogen iodide that are produced. The mole ratio of H₂:I₂:HI = 1:1:2, therefore the number of moles of HI produced is $0.1735 \times 2 = 0.347$ mol.

So far, the table can be filled in as follows:

	H_2 (g)	I_2	2HI
Start of reaction	0.496	0.181	0
Used up	0.1735	0.1735	0
Produced	0	0	0.347
Equilibrium	0.3225	0.0075	0.347

Step 4 : Calculate the concentration of each of the reactants and products at equilibrium.

$$c = \frac{n}{V}$$

C

Therefore the equilibrium concentrations are as follows: $[H_2] = 0.3225 \text{ mol.dm}^{-3} \\ [I_2] = 0.0075 \text{ mol.dm}^{-3} \\ [HI] = 0.347 \text{ mol.dm}^{-3}$

Step 5 : Calculate k_c

$$k_c = \frac{[HI]}{[H_2][I_2]} = \frac{0.347}{0.3225 \times 0.0075} = 143.47$$

Exercise: The equilibrium constant

- 1. Write the equilibrium constant expression, K_c for the following reactions:
 - (a) $2NO(g) + Cl_2(g) \Leftrightarrow 2NOCl$
 - (b) $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$
- 2. The following reaction takes place:

$$Fe^{3+}(aq) + 4Cl^{-} \Leftrightarrow FeCl_{4}^{-}(aq)$$

 ${\sf K}_c$ for the reaction is 7.5 \times 10 $^{-2}$ mol.dm $^{-3}.$ At equilibrium, the concentration of FeCl_4^- is 0.95 \times 10 $^{-4}$ mol.dm $^{-3}$ and the concentration of free iron (Fe $^{3+}$) is 0.2 mol.dm $^{-3}$. Calculate the concentration of chloride ions at equilibrium.

3. Ethanoic acid (CH₃COOH) reacts with ethanol (CH₃CH₂OH) to produce ethyl ethanoate and water. The reaction is:

 $CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + H_2O$

At the beginning of the reaction, there are 0.5 mols of ethanoic acid and 0.5 mols of ethanol. At equilibrium, 0.3 mols of ethanoic acid was left unreacted. The volume of the reaction container is 2 dm³. Calculate the value of K_c.

16.8 Le Chatelier's principle

A number of factors can influence the equilibrium of a reaction. These are:

- 1. concentration
- 2. temperature
- 3. pressure

Le Chatelier's Principle helps to predict what a change in temperature, concentration or pressure will have on the position of the equilibrium in a chemical reaction. This is very important, particularly in industrial applications, where yields must be accurately predicted and maximised.



Definition: Le Chatelier's Principle

If a chemical system at equilibrium experiences a change in concentration, temperature or total pressure the equilibrium will shift in order to minimise that change.

16.8.1 The effect of concentration on equilibrium

If the concentration of a substance is increased, the equilibrium will shift so that this concentration decreases. So for example, if the concentration of a reactant was increased, the equilibrium would shift in the direction of the reaction that *uses up* the reactants, so that the reactant concentration decreases and equilibrium is restored. In the reaction between nitrogen and hydrogen to produce ammonia:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

- If the nitrogen or hydrogen concentration was increased, Le Chatelier's principle predicts that equilibrium will shift to favour the *forward reaction* so that the excess nitrogen and hydrogen are used up to produce ammonia. Equilibrium shifts to the *right*.
- If the nitrogen or hydrogen concentration was decreased, the *reverse reaction* would be favoured so that some of the ammonia would change back to nitrogen and hydrogen to restore equilibrium.
- The same would be true if the concentration of the product (NH₃) was changed. If [NH₃] decreases, the forward reaction is favoured and if [NH₃] increases, the reverse reaction is favoured.

16.8.2 The effect of temperature on equilibrium

If the temperature of a reaction mixture is increased, the equilibrium will shift to decrease the temperature. So it will favour the reaction which will *use up* heat energy, in other words the endothermic reaction. The opposite is true if the temperature is decreased. In this case, the reaction that *produces* heat energy will be favoured, in other words, the exothermic reaction.

The reaction shown below is exothermic (shown by the negative value for Δ H). This means that the forward reaction, where nitrogen and hydrogen react to form ammonia, gives off heat. In the reverse reaction, where ammonia is broken down into hydrogen and nitrogen gas, heat is used up and so this reaction is endothermic.

e.g.
$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$
 and $\Delta H = -92kJ$

An increase in temperature favours the reaction that is endothermic (the reverse reaction) because it uses up energy. If the temperature is increased, then the yield of ammonia (NH_3)
decreases.

A decrease in temperature favours the reaction that is exothermic (the forward reaction) because it produces energy. Therefore, if the temperature is decreased, then the yield of NH_3 increases.

Activity :: Experiment : Le Chatelier's Principle Aim:

To determine the effect of a change in concentration and temperature on chemical equilibrium

Apparatus:

 $0.2\ M\ CoCl_2$ solution, concentrated HCl, water, test tube, bunsen burner Method:

- 1. Put 4-5 drops of 0.2M $CoCl_2$ solution into a test tube.
- 2. Add 20-25 drops of concentrated HCI.
- 3. Add 10-12 drops of water.
- 4. Heat the solution for 1-2 minutes.
- 5. Cool the solution for 1 minute under a tap.
- 6. Observe and record the colour changes that take place during the reaction.

The equation for the reaction that takes place is:

e.g.
$$\underbrace{CoCl_4^{2-} + 6H_2O}_{\text{blue}} \Leftrightarrow \underbrace{Co(H_2O)_6^{2+} + 4Cl^-}_{\text{pink}}$$

Results:

Complete your observations in the table below, showing the colour changes that take place, and also indicating whether the concentration of each of the ions in solution increases or decreases.

	Initial colour	Final colour	[Co ²⁺]	[CI [−]]	$[CoCl_4^{2-}]$
Add CI^-					
Add H_2O					
Increase					
temp.					
Decrease					
temp.					

Conclusions:

Use your knowledge of equilibrium principles to explain the changes that you recorded in the table above. Draw a conclusion about the effect of a change in concentration of either the reactants or products on the equilibrium position. Also draw a conclusion about the effect of a change in temperature on the equilibrium position.

16.8.3 The effect of pressure on equilibrium

In the case of gases, we refer to pressure instead of concentration. Similar principles apply as those that were described before for concentration. When the pressure of a system increases, there are more particles in a particular space. The equilibrium will shift in a direction that reduces the number of gas particles so that the pressure is also reduced. To predict what will happen in a reaction, we need to look at the number of moles of gas that are in the reactants and products. Look at the example below:

e.g. $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$

In this reaction, two moles of product are formed for every three moles of reactants. If we increase the pressure on the closed system, the equilibrium will shift to the right because the forward reaction reduces the number of moles of gas that are present. This means that the yield of SO_3 will increase. The opposite will apply if the pressure on the system decreases. the equilibrium will shift to the left, and the concentration of SO_2 and O_2 will increase.



Important: The following rules will help in predicting the changes that take place in equilibrium reactions:

- 1. If the forward reaction that forms the product is endothermic, then an increase in temperature will favour this reaction and the yield of product will increase. Lowering the temperature will decrease the product yield.
- 2. If the forward reaction that forms the product is exothermic, then a decrease in temperature will favour this reaction and the product yield will increase. Increasing the temperature will decrease the product yield.
- 3. Increasing the pressure favours the side of the equilibrium with the least number of gas molecules. This is shown in the balanced symbol equation. This rule applies in reactions with one or more gaseous reactants or products.
- Decreasing the pressure favours the side of the equilibrium with the most number of gas molecules. This rule applies in reactions with one or more gaseous reactants or products.
- 5. If the concentration of a reactant (on the left) is increased, then some of it must change to the products (on the right) for equilibrium to be maintained. The equilibrium position will shift to the right.
- 6. If the concentration of a reactant (on the left) is decreased, then some of the products (on the right) must change back to reactants for equilibrium to be maintained. The equilibrium position will shift to the left.
- 7. A **catalyst** does not affect the equilibrium position of a reaction. It only influences the *rate of the reaction*, in other words, how quickly equilibrium is reached.



Worked Example 81: Reaction Rates 1

Question: $2NO_2(g) \Leftrightarrow 2NO(g) + O_2(g)$ and $\Delta H > 0$ How will the rate of the reverse reaction be affected by:

- 1. a decrease in temperature?
- 2. the addition of a catalyst?
- 3. the addition of more NO gas?

Answer

- 1. The rate of the forward reaction will increase since it is the forward reaction that is exothermix and therefore *produces* energy to balance the loss of energy from the decrease in temperature. The rate of the reverse reaction will decrease.
- 2. The rate of the reverse and the forward reaction will increase.
- 3. The rate of the reverse reaction will increase so that the extra NO gas is converted into NO_2 gas.



Worked Example 82: Reaction Rates 2

Question:

- 1. Write a balanced equation for the exothermic reaction between Zn(s) and HCl.
- Name 3 ways to increase the reaction rate between hydrochloric acid and zinc metal.

Answer

- 1. $Zn(s) + 2HCl(aq) \Leftrightarrow ZnCl_2(aq) + H_2(g)$
- 2. A catalyst could be added, the zinc solid could be ground into a fine powder to increase its surface area, the HCI concentration could be increased or the reaction temperature could be increased.



Exercise: Reaction rates and equilibrium

1. The following reaction reaches equilibrium in a closed container:

 $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$

The pressure of the system is increased by decreasing the volume of the container. How will the number of moles and the concentration of the $CO_2(g)$ have changed when a new equilibrium is reached at the same temperature?

	moles of CO_2	[CO ₂]
А	decreased	decreased
В	increased	increased
C	decreased	stays the same
D	decreased	increased

(IEB Paper 2, 2003)

2. The following reaction has reached equilibrium in a closed container:

$$C(s) + H_2O(g) \Leftrightarrow CO(g) + H_2(g) \Delta H \downarrow 0$$

The pressure of the system is then decreased by increasing the volume of the container. How will the concentration of the $H_2(g)$ and the value of K_c be affected when the new equilibrium is established? Assume that the temperature of the system remains unchanged.

	$[H_2]$	K_{c}
Α	increases	increases
В	increases	unchanged
С	unchanged	unchanged
D	decreases	unchanged

(IEB Paper 2, 2004)

3. During a classroom experiment copper metal reacts with concentrated nitric acid to produce NO₂ gas, which is collected in a gas syringe. When enough gas has collected in the syringe, the delivery tube is clamped so that no gas can escape. The brown NO₂ gas collected reaches an equilibrium with colourless N_2O_4 gas as represented by the following equation:

$$2NO_2(g) \Leftrightarrow N_2O_4(g)$$

Once this equilibrium has been established, there are 0.01 moles of NO $_2$ gas and 0.03 moles of N $_2O_4$ gas present in the syringe.

- (a) A learner, noticing that the colour of the gas mixture in the syringe is no longer changing, comments that all chemical reactions in the syringe must have stopped. Is this assumption correct? Explain.
- (b) The gas in the syringe is cooled. The volume of the gas is kept constant during the cooling process. Will the gas be lighter or darker at the lower temperature? Explain your answer.
- (c) The volume of the syringe is now reduced to 75 cm³ by pushing the plunger in and holding it in the new position. There are 0.032 moles of N_2O_4 gas present once the equilibrium has been re-established at the reduced volume (75 cm³). Calculate the value of the equilibrium constant for this equilibrium.

(IEB Paper 2, 2004)

4. Consider the following reaction, which takes place in a closed container:

$$A(s) + B(g) \rightarrow AB(g) \Delta H < 0$$

If you wanted to increase the rate of the reaction, which of the following would you do?

- (a) decrease the concentration of B
- (b) decrease the temperature of A
- (c) grind A into a fine powder
- (d) decrease the pressure

(IEB Paper 2, 2002)

5. Gases X and Y are pumped into a 2 dm^3 container. When the container is sealed, 4 moles of gas X and 4 moles of gas Y are present. The following equilibrium is established:

$$2X(g) + 3Y(g) \Leftrightarrow X_2Y_3$$

The graph below shows the number of moles of gas X and gas X_2Y_3 that are present from the time the container is sealed.



- (a) How many moles of gas X_2Y_3 are formed by the time the reaction reaches equilibrium at 30 seconds?
- (b) Calculate the value of the equilibrium constant at t = 50 s.
- (c) At 70 s the temperature is increased. Is the forward reaction endothermic or exothermic? Explain in terms of Le Chatelier's Principle.
- (d) How will this increase in temperature affect the value of the equilibrium constant?

16.9 Industrial applications

The **Haber process** is a good example of an industrial process which uses the equilibrium principles that have been discussed. The equation for the process is as follows:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) + energy$$

Since the reaction is **exothermic**, the forward reaction is favoured at low temperatures, and the reverse reaction at high temperatures. If the purpose of the Haber process is to produce ammonia, then the temperature must be maintained at a level that is low enough to ensure that the reaction continues in the forward direction.

The forward reaction is also favoured by high *pressures* because there are four moles of reactant for every two moles of product formed.

The k value for this reaction will be calculated as follows:

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

?

Exercise: Applying equilibrium principles

Look at the values of k calculated for the Haber process reaction at different temperatures, and then answer the questions that follow:

T^{oC}	k
25	6.4×10^2
200	4.4×10^{-1}
300	4.3×10^{-3}
400	1.6×10^{-4}
500	1.5×10^{-5}

- 1. What happens to the value of k as the temperature increases?
- 2. Which reaction is being favoured when the temperature is 300 degrees celsius?
- 3. According to this table, which temperature would be best if you wanted to produce as much ammonia as possible? Explain.

16.10 Summary

- The **rate of a reaction** describes how quickly reactants are used up, or how quickly products form. The units used are moles per second.
- A number of factors can affect the rate of a reaction. These include the **nature of the reactants**, the **concentration** of reactants, **temperature** of the reaction, the presence or absence of a **catalyst** and the **surface area** of the reactants.
- **Collision theory** provides one way of explaining why each of these factors can affect the rate of a reaction. For example, higher temperatures mean increased reaction rates because the reactant particles have more energy and are more likely to collide successfully with each other.
- Different methods can be used to **measure the rate of a reaction**. The method used will depend on the nature of the product. Reactions that produce gases can be measured by collecting the gas in a syringe. Reactions that produce a precipitate are also easy to measure because the precipitate is easily visible.
- For any reaction to occur, a minimum amount of energy is needed so that bonds in the reactants can break, and new bonds can form in the products. The minimum energy that is required is called the **activation energy** of a reaction.
- In reactions where the particles do not have enough energy to overcome this activation energy, one of two methods can be used to facilitate a reaction to take place: increase the temperature of the reaction or add a catalyst.
- Increasing the temperature of a reaction means that the average energy of the reactant particles increases and they are more likely to have enough energy to overcome the activation energy.
- A **catalyst** is used to lower the activation energy so that the reaction is more likely to take place. A catalyst does this by providing an alternative, lower energy pathway, for the reaction.
- A catalyst therefore **speeds up a reaction** but does not become part of the reaction in any way.
- **Chemical equilibrium** is the state of a reaction, where the concentrations of the reactants and the products have no net change over time. Usually this occurs when the rate of the forward reaction is the same as the rate of the reverse reaction.
- The **equilibrium constant** relates to reactions at equilibrium, and can be calculated using the following equation:

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

where A and B are reactants, C and D are products and a, b, c, and d are the coefficients of the respective reactants and products.

- A high k_c value means that the concentration of products at equilibrium is high and the reaction has a high yield. A low k_c value means that the concentration of products at equilibrium is low and the reaction has a low yield.
- Le Chatelier's Principle states that if a chemical system at equilibrium experiences a change in concentration, temperature or total pressure the equilibrium will shift in order to minimise that change. For example, if the pressure of a gaseous system at eqilibrium was increased, the equilibrium would shift to favour the reaction that produces the lowest quantity of the gas. If the temperature of the same system was to increase, the equilibrium would shift to favour the endothermic reaction. Similar principles apply for changes in concentration of the reactants or products in a reaction.
- The principles of equilibrium are very important in **industrial applications** such as the Haber process, so that productivity can be maximised.

Exercise: Summary Exercise

- 1. For each of the following questions, choose the one correct answer from the list provided.
 - (a) Consider the following reaction that has reached equilibrium after some time in a sealed 1 dm³ flask:

 $PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g); \Delta H$ is positive

Which one of the following reaction conditions applied to the system would decrease the rate of the reverse reaction?

- i. increase the pressure
- ii. increase the reaction temperature
- iii. continually remove $Cl_2(g)$ from the flask
- iv. addition of a suitable catalyst

(IEB Paper 2, 2001)

(b) The following equilibrium constant expression is given for a particular reaction:

$$K_c = [H_2 O]^4 [CO_2]^3 / [C_3 H_8] [O_2]^5$$

For which one of the following reactions is the above expression of K_c is correct?

- i. $C_3H_8(g) + 5O_2(g) \Leftrightarrow 4H_2O(g) + 3CO_2(g)$
- ii. $4H_2O(g) + 3CO_2(g) \Leftrightarrow C_3H_8(g) + 5O_2(g)$
- iii. $2C_3H_8(g) + 7O_2(g) \Leftrightarrow 6CO(g) + 8H_2O(g)$
- iv. $C_3H_8(g) + 5O_2(g) \Leftrightarrow 4H_2O(l) + 3CO_2(g)$

(IEB Paper 2, 2001)

- 2. 10 g of magnesium ribbon reacts with a 0.15 mol.dm $^{-3}$ solution of hydrochloric acid at a temperature of 25 $^{0}{\rm C}.$
 - (a) Write a balanced chemical equation for the reaction.
 - (b) State **two** ways of increasing the rate of production of $H_2(g)$.
 - (c) A table of the results is given below:

Time elapsed (min)	Vol of $H_2(g)$ (cm ³)
0	0
0.5	17
1.0	25
1.5	30
2.0	33
2.5	35
3.0	35

- i. Plot a graph of volume versus time for these results.
- ii. Explain the shape of the graph during the following two time intervals: t = 0 to t = 2.0 min and then t = 2.5 and t = 3.0 min by referring to the volume of H₂(g) produced.

(IEB Paper 2, 2001)

3. Cobalt chloride crystals are dissolved in a beaker containing ethanol and then a few drops of water are added. After a period of time, the reaction reaches equilibrium as follows:

$$CoCl_4^{2-}$$
 (blue) $+6H_2O \Leftrightarrow Co(H_2O)_6^{2+}$ (pink) $+4Cl^{-}$

The solution, which is now just blue, is poured into three test tubes. State, in each case, what colour changes will be observed (if any) if the following are added in turn to each test tube:

- (a) 1 cm^3 of distilled water
- (b) A few crystals of sodium chloride

(c) The addition of dilute hydrochloric acid to the third test tube causes the solution to turn pink. Explain why this occurs.

(IEB Paper 2, 2001)

Chapter 17

Electrochemical Reactions - Grade 12

17.1 Introduction

Chapter 15 in Grade 11 discussed *oxidation*, *reduction* and *redox reactions*. **Oxidation** involves a **loss of electrons** and **reduction** involves a **gain of electrons**. A **redox reaction** is a reaction where both oxidation and reduction take place. What is common to all of these processes is that they involve a *transfer of electrons* and a change in the oxidation state of the elements that are involved.



Exercise: Oxidation and reduction

- 1. Define the terms oxidation and reduction.
- 2. In each of the following reactions say whether the **iron** in the reactants is oxidised or reduced.
 - (a) $Fe \rightarrow Fe^{2+} + 2e^{-}$
 - (b) $Fe^{3+} + e^- \to Fe^{2+}$
 - (c) $Fe_2O_3 \rightarrow Fe$
 - (d) $Fe^{2+} \to Fe^{3+} + e^{-}$
 - (e) $Fe_2O_3 + 2Al \rightarrow Al_2$
- 3. In each of the following equations, say which elements in the reactants are oxidised and which are reduced.
 - (a) $CuO(s) + H_2(g) \to Cu(s) + H_2O(g)$
 - (b) $2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$
 - (c) $Mg(s) + FeSO_4(aq) \rightarrow MgSO_4(aq) + Fe(s)$
 - (d) $Zn(s) + 2AgNO_3(aq) \rightarrow 2Ag + Zn(NO_3)_2(aq)$
- 4. Which one of the substances listed below acts as the oxidising agent in the following reaction?

$$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$$

- (a) H⁺
- (b) Cr^{3+}
- (c) SO₂
- (d) $Cr_2O_7^{2-}$

In Grade 11, an experiment was carried out to see what happened when zinc granules are added to a solution of copper(II) sulphate. In the experiment, the Cu^{2+} ions from the copper(II) sulphate solution were reduced to copper metal, which was then deposited in a layer on the zinc granules. The zinc atoms were oxidised to form Zn^{2+} ions in the solution. The half reactions are as follows:

 $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (reduction half reaction) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation half reaction)

The overall redox reaction is:

$$Cu^{2+}(aq) + Zn \rightarrow Cu(s) + Zn^{2+}(aq)$$

There was an increase in the temperature of the reaction when you carried out this experiment. Is it possible that this heat energy could be converted into electrical energy? In other words, can we use a chemical reaction where there is an exchange of electrons, to produce electricity? And if this is possible, what would happen if an electrical current was supplied to *cause* some type of chemical reaction to take place?

An **electrochemical reaction** is a chemical reaction that *produces a voltage*, and therefore a flow of electrical current. An electrochemical reaction can also be the reverse of this process, in other words if an electrical current causes a chemical reaction to take place.



Definition: Electrochemical reaction

If a chemical reaction is caused by an external voltage, or if a voltage is caused by a chemical reaction, it is an electrochemical reaction.

Electrochemistry is the branch of chemistry that studies these electrochemical reactions. In this chapter, we will be looking more closely at different types of electrochemical reactions, and how these can be used in different ways.

17.2 The Galvanic Cell

Activity :: Experiment : Electrochemical reactions Aim:

To investigate the reactions that take place in a zinc-copper cell **Apparatus:**

zinc plate, copper plate, measuring balance, zinc sulphate (ZnSO₄) solution (1 mol.dm⁻³), copper sulphate (CuSO₄) solution (1 mol.dm⁻³), two 250 ml beakers, U-tube, Na₂SO₄ solution, cotton wool, ammeter, connecting wire. **Method:**

- 1. Measure the mass of the copper and zinc plates and record your findings.
- 2. Pour about 200 ml of the zinc sulphate solution into a beaker and put the zinc plate into it.
- 3. Pour about 200 ml of the copper sulphate solution into the second beaker and place the copper plate into it.
- 4. Fill the U-tube with the Na_2SO_4 solution and seal the ends of the tubes with the cotton wool. This will stop the solution from flowing out when the U-tube is turned upside down.

- 5. Connect the zinc and copper plates to the ammeter and observe whether the ammeter records a reading.
- 6. Place the U-tube so that one end is in the copper sulphate solution and the other end is in the zinc sulphate solution. Is there a reading on the ammeter? In which direction is the current flowing?
- 7. Take the ammeter away and connect the copper and zinc plates to each other directly using copper wire. Leave to stand for about one day.
- 8. After a day, remove the two plates and rinse them first with distilled water, then with alcohol and finally with ether. Dry the plates using a hair dryer.
- 9. Weigh the zinc and copper plates and record their mass. Has the mass of the plates changed from the original measurements?

Note: A voltmeter can also be used in place of the ammeter. A voltmeter will measure the potential difference across the cell.



Results:

During the experiment, you should have noticed the following:

- \bullet When the U-tube containing the Na_2SO_4 solution was absent, there was no reading on the ammeter.
- When the U-tube was connected, a reading was recorded on the ammeter.
- After the plates had been connected directly to each other and left for a day, there was a change in their mass. The mass of the zinc plate decreased, while the mass of the copper plate increased.
- The direction of electron flow is from the zinc plate towards the copper plate.

Conclusions:

When a zinc sulphate solution containing a zinc plate is connected by a U-tube to a copper sulphate solution containing a copper plate, reactions occur in both solutions. The decrease in mass of the zinc plate suggests that the zinc metal has been oxidised. The increase in mass of the copper plate suggests that reduction has occurred here to produce more copper metal. This will be explained in detail below.

17.2.1 Half-cell reactions in the Zn-Cu cell

The experiment above demonstrated a zinc-copper cell. This was made up of a zinc half cell and a copper half cell.

17.2

Definition: Half cell

A half cell is a structure that consists of a conductive electrode surrounded by a conductive electrolyte. For example, a zinc half cell could consist of a zinc metal plate (the electrode) in a zinc sulphate solution (the electrolyte).

How do we explain what has just been observed in the zinc-copper cell?

• Copper plate

At the copper plate, there was an *increase* in mass. This means that Cu^{2+} ions from the copper sulphate solution were deposited onto the plate as atoms of copper metal. The half-reaction that takes place at the copper plate is:

 $Cu^{2+} + 2e^- \rightarrow Cu$ (Reduction half reaction)

Another shortened way to represent this copper half-cell is Cu^{2+}/Cu .

• Zinc plate

At the zinc plate, there was a *decrease* in mass. This means that some of the zinc goes into solution as Z^{2+} ions. The electrons remain on the zinc plate, giving it a negative charge. The half-reaction that takes place at the zinc plate is:

 $Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation half reaction)

The shortened way to represent the zinc half-cell is Zn/Zn^{2+} .

The overall reaction is:

 $Zn+Cu^{2+}+2e^-\to Zn^{2+}+Cu+2e^-$ or, if we cancel the electrons: $Zn+Cu^{2+}\to Zn^{2+}+Cu$

For this electrochemical cell, the standard notation is:

$$Zn|Zn^{2+}||Cu^{2+}|Cu$$

where

= a phase boundary (solid/aqueous)
 = the salt bridge

In the notation used above, the oxidation half-reaction at the anode is written on the left, and the reduction half-reaction at the cathode is written on the right. In the Zn-Cu electrochemical cell, the direction of current flow in the external circuit is from the zinc electrode (where there has been a build up of electrons) to the copper electrode.

17.2.2 Components of the Zn-Cu cell

In the zinc-copper cell, the copper and zinc plates are called the **electrodes**. The electrode where oxidation occurs is called the **anode**, and the electrode where reduction takes place is called the **cathode**. In the zinc-copper cell, the zinc plate is the anode and the copper plate is the cathode.



Definition: Electrode

An electrode is an electrical conductor that is used to make contact with a metallic part of a circuit. The anode is the electrode where oxidation takes place. The cathode is the electrode where reduction takes place. The zinc sulphate and copper sulphate solutions are called the **electrolyte** solutions.



Definition: Electrolyte

An electrolyte is a substance that contains free ions and which therefore behaves as an electrical conductor.

The U-tube also plays a very important role in the cell. In the Zn/Zn²⁺ half-cell, there is a build up of positive charge because of the release of electrons through oxidation. In the Cu²⁺/Cu half-cell, there is a decrease in the positive charge because electrons are gained through reduction. This causes a movement of SO_4^{2-} ions into the beaker where there are too many positive ions, in order to neutralise the solution. Without this, the flow of electrons in the outer circuit stops completely. The U-tube is called the **salt bridge**. The salt bridge acts as a transfer medium that allows ions to flow through without allowing the different solutions to mix and react.



Definition: Salt bridge

A salt bridge, in electrochemistry, is a laboratory device that is used to connect the oxidation and reduction half-cells of a galvanic cell.

17.2.3 The Galvanic cell

In the zinc-copper cell the important thing to notice is that the chemical reactions that take place at the two electrodes cause an electric current to flow through the outer circuit. In this type of cell, **chemical energy is converted to electrical energy**. These are called **galvanic cells**. The zinc-copper cell is one example of a galvanic cell. A galvanic cell (which is also sometimes referred to as a **voltaic** or **electrochemical** cell) consists of two metals that are connected by a salt bridge between the individual half-cells. A galvanic cell generates electricity using the reactions that take place at these two metals, each of which has a different **reaction potential**.

So what is meant by the 'reaction potential' of a substance? Every metal has a different half reaction and different dissolving rates. When two metals with different reaction potentials are used in a galvanic cell, a potential difference is set up between the two electrodes, and the result is a flow of current through the wire that connects the electrodes. In the zinc-copper cell, zinc has a higher reaction potential than copper and therefore dissolves more readily into solution. The metal 'dissolves' when it loses electrons to form positive metal ions. These electrons are then transferred through the connecting wire in the outer circuit.



Definition: Galvanic cell

A galvanic (voltaic) cell is an electrochemical cell that uses a chemical reaction between two dissimilar electrodes dipped in an electrolyte, to generate an electric current.



It was the Italian physician and anatomist Luigi Galvani who marked the birth of electrochemistry by making a link between chemical reactions and electricity. In 1780, Galvani discovered that when two different metals (copper and zinc for example) were connected together and then both touched to different parts of a nerve of a frog leg at the same time, they made the leg contract. He called this "animal electricity". While many scientists accepted his ideas, another scientist, Alessandro Volta, did not. In 1800, because of his professional disagreement over the galvanic response that had been suggested by Luigi Galvani, Volta developed the *voltaic pile*, which was very similar to the galvanic cell. It was the work of these two men that paved the way for all electrical batteries.

Worked Example 83: Understanding galvanic cells

Question: For the following cell:

$$Zn|Zn^{2+}||Ag^+|Ag|$$

- 1. Give the anode and cathode half-reactions.
- 2. Write the overall equation for the chemical reaction.
- 3. Give the direction of the current in the external circuit.

Answer

Step 1 : Identify the oxidation and reduction reactions

In the standard notation format, the oxidation reaction is written on the left and the reduction reaction on the right. So, in this cell, zinc is oxidised and silver ions are reduced.

Step 2 : Write the two half reactions

Oxidation half-reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$

Reduction half-reaction: $Ag^+ + e^- \rightarrow Ag$

Step 3 : Combine the half-reactions to get the overall equation.

When you combine the two half-reactions, all the reactants must go on the left side of the equation and the products must go on the right side of the equation. The overall equation therefore becomes:

 $\mathrm{Zn} + \mathrm{Ag}^+ + \mathrm{e}^- \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^- + \mathrm{Ag}$

Note that this equation is not balanced. This will be discussed later in the chapter.

Step 4 : Determine the direction of current flow

A build up of electrons occurs where oxidation takes place. This is at the zinc electrode. Current will therefore flow from the zinc electrode to the silver electrode.

17.2.4 Uses and applications of the galvanic cell

The principles of the galvanic cell are used to make **electrical batteries**. In science and technology, a battery is a device that stores chemical energy and makes it available in an electrical form. Batteries are made of electrochemical devices such as one or more galvanic cells, fuel cells or flow cells. Batteries have many uses including in torches, electrical appliances (long-life alkaline batteries), digital cameras (lithium battery), hearing aids (silver-oxide battery), digital watches (mercury battery) and military applications (thermal battery). Refer to chapter 23 for more information on batteries.

The galvanic cell can also be used for **electroplating**. Electroplating occurs when an electrically conductive object is coated with a layer of metal using electrical current. Sometimes, electroplating is used to give a metal particular properties such as corrosion protection or wear resistance. At other times, it can be for aesthetic reasons for example in the production of jewellery. This will be discussed in more detail later in this chapter.

Exercise: Galvanic cells

1. The following half-reactions take place in an electrochemical cell:

 $Fe \rightarrow Fe^{3+} + 3e^{-}$ $Fe^{2+} + 2e^{-} \rightarrow Fe^{-}$

- (a) Which is the oxidation half-reaction?
- (b) Which is the reduction half-reaction?
- (c) Name one oxidising agent.
- (d) Name one reducing agent.
- (e) Use standard notation to represent this electrochemical cell.
- 2. For the following cell:

$$Mg|Mg^{2+}||Mn^{2+}|Mn$$

- (a) Give the cathode half-reaction.
- (b) Give the anode half-reaction.
- (c) Give the overall equation for the electrochemical cell.
- (d) What metals could be used for the electrodes in this electrochemical cell.
- (e) Suggest two electrolytes for this electrochemical cell.
- (f) In which direction will the current flow?
- (g) Draw a simple sketch of the complete cell.
- 3. For the following cell:

$$Sn|Sn^{2+}||Ag^{+}|Ag$$

- (a) Give the cathode half-reaction.
- (b) Give the anode half-reaction.
- (c) Give the overall equation for the electrochemical cell.
- (d) Draw a simple sketch of the complete cell.

17.3 The Electrolytic cell

In section 17.2, we saw that a chemical reaction that involves a transfer of electrons, can be used to produce an electric current. In this section, we are going to see whether the 'reverse' process applies. In other words, is it possible to use an electric current to force a particular chemical reaction to occur, which would otherwise not take place? The answer is 'yes', and the type of cell that is used to do this, is called an **electrolytic cell**.



Definition: Electrolytic cell

An electrolytic cell is a type of cell that uses electricity to drive a non-spontaneous reaction.

An electrolytic cell is activated by applying an electrical potential across the anode and cathode to force an internal chemical reaction between the ions that are in the electrolyte solution. This process is called **electrolysis**.



Definition: Electrolysis

In chemistry and manufacturing, electrolysis is a method of separating bonded elements and compounds by passing an electric current through them.

Activity :: Demonstration : The movement of coloured ions

A piece of filter paper is soaked in an ammonia-ammonium chloride solution and placed on a microscope slide. The filter paper is then connected to a supply of electric current using crocodile clips and connecting wire as shown in the diagram below. A line of copper chromate solution is placed in the centre of the filter paper. The colour of this solution is initially green-brown.



The current is then switched on and allowed to run for about 20 minutes. After this time, the central coloured band disappears and is replaced by two bands, one yellow and the other blue, which seem to have separated out from the first band of copper chromate.

Explanation:

- The cell that is used to supply an electric current sets up a potential difference across the circuit, so that one of the electrodes is positive and the other is negative.
- The chromate (CrO_4^{2-}) ions in the copper chromate solution are attracted to the positive electrode, while the Cu²⁺ ions are attracted to the negative electrode.

Conclusion:

The movement of ions occurs because the electric current in the outer circuit sets up a potential difference between the two electrodes.

Similar principles apply in the electrolytic cell, where substances that are made of ions can be broken down into simpler substances through electrolysis.

17.3.1 The electrolysis of copper sulphate

There are a number of examples of electrolysis. The electrolysis of copper sulphate is just one.

Activity :: Demonstration : The electrolysis of copper sulphate

Two copper electrodes are placed in a solution of blue copper sulphate and are connected to a source of electrical current as shown in the diagram below. The current is turned on and the reaction is left for a period of time.



Observations:

- The initial blue colour of the solution remains unchanged.
- It appears that copper has been *deposited* on one of the electrodes but *dissolved* from the other.

Explanation:

• At the negative cathode, positively charged Cu²⁺ ions are attracted to the negatively charged electrode. These ions gain electrons and are reduced to form copper metal, which is deposited on the electrode. The half-reaction that takes place is as follows:

 $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ (reduction half reaction)

• At the positive anode, copper metal is oxidised to form Cu^{2+} ions. This is why it appears that some of the copper has dissolved from the electrode. The half-reaction that takes place is as follows:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$
 (oxidation half reaction)

• The amount of copper that is *deposited* at one electrode is approximately the same as the amount of copper that is *dissolved* from the other. The number of Cu^{2+} ions in the solution therefore remains almost the same and the blue colour of the solution is unchanged.

Conclusion:

In this demonstration, an electric current was used to split $CuSO_4$ into its component ions, Cu^{2+} and SO_4^{2-} . This process is called *electrolysis*.

17.3.2 The electrolysis of water

Water can also undergo electrolysis to form hydrogen gas and oxygen gas according to the following reaction:

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

This reaction is very important because hydrogen gas has the potential to be used as an energy source. The electrolytic cell for this reaction consists of two electrodes (normally platinum metal), submerged in an electrolyte and connected to a source of electric current.

The reduction half-reaction that takes place at the cathode is as follows:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

The oxidation half-reaction that takes place at the anode is as follows:

$$2H_2O(l) \to O_2(g) + 4H^+(aq) + 4e^-$$

17.3.3 A comparison of galvanic and electrolytic cells

It should be much clearer now that there are a number of differences between a *galvanic* and an *electrolytic* cell. Some of these differences have been summarised in table 17.1.

ltem	Galvanic cell	Electrolytic cell
Metals used for electrode	Two metals with different	The same metal can be
	reaction potentials are used	used for both the cathode
	as electrodes	and the anode
Charge of the anode	negative	positive
Charge of the cathode	positive	negative
The electrolyte solution/s	The electrolyte solutions	The cathode and anode are
	are kept separate from one	in the same electrolyte
	another, and are connected	
	only by a salt bridge	
Energy changes	Chemical potential energy	An external supply of elec-
	from chemical reactions is	trical energy causes a chem-
	converted to electrical en-	ical reaction to occur
	ergy	
Applications	Run batteries, electroplat-	Electrolysis e.g. of water,
	ing	NaCl

Table 17.1: A comparison of galvanic and electrolytic cells



Exercise: Electrolyis

- 1. An electrolytic cell consists of two electrodes in a silver chloride (AgCl) solution, connected to a source of current. A current is passed through the solution and
 - Ag^+ ions are reduced to a silver metal deposit on one of the electrodes.
 - (a) Give the equation for the reduction half-reaction.
 - (b) Give the equation for the oxidation half-reacion.
- 2. Electrolysis takes place in a solution of molten lead bromide (PbBr) to produce lead atoms.
 - (a) Draw a simple diagram of the electrolytic cell.
 - (b) Give equations for the half-reactions that take place at the anode and cathode, and include these in the diagram.
 - (c) On your diagram, show the direction in which current flows.

17.4 Standard Electrode Potentials

If a voltmeter is connected in the circuit of an electrochemical cell, a reading is obtained. In other words, there is a **potential difference** between the two half cells. In this section, we are going to look at this in more detail to try to understand more about the **electrode potentials** of each of the electrodes in the cell. We are going to break this section down so that you build up your understanding gradually. Make sure that you understand each subsection fully before moving on, otherwise it might get confusing!

17.4.1 The different reactivities of metals

All metals have different reactivities. When metals react, they give away electrons and form positive ions. But some metals do this more easily than others. Look at the following two half reactions:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

 $Cu \rightarrow Cu^{2+} + 2e^{-}$

Of these two metals, zinc is more reactive and is more likely to give away electrons to form Zn^{2+} ions in solution, than is copper.

17.4.2 Equilibrium reactions in half cells

Let's think back to the Zn-Cu electrochemical cell. This cell is made up of two half cells and the reactions that take place at each of the electrodes are as follows:

$$Zn \to Zn^{2+} + 2e^{-}$$
$$Cu^{2+} + 2e^{-} \to Cu$$

At the zinc electrode, the zinc metal loses electrons and forms Zn^{2+} ions. The electrons are concentrated on the zinc metal while the Zn^{2+} ions are in solution. But some of the ions will be attracted back to the negatively charged metal, will gain their electrons again and will form zinc metal. A **dynamic equilibrium** is set up between the zinc metal and the Zn^{2+} ions in solution when the rate at which ions are *leaving* the metal is equal to the rate at which they are *joining* it again. The situation looks something like the diagram in figure 17.1.



zinc metal

 Zn^{2+} ions in solution

concentration of electrons on metal surface

Figure 17.1: Zinc loses electrons to form positive ions in solution. The electrons accumulate or the metal surface.

The equilibrium reaction is represented like this:

$$Zn^{2+}(aq) + 2e^{-} \Leftrightarrow Zn(s)$$

(NOTE: By convention, the ions are written on the *left* hand side of the equation)

2

In the zinc half cell, the equilibrium lies far to the left because the zinc loses electrons easily to form Zn^{2+} ions. We can also say that the zinc is *oxidised* and that it is a strong *reducing agent*.

At the copper electrode, a similar process takes place. The difference though is that copper is not as reactive as zinc and so it does not form ions as easily. This means that the build up of electrons on the copper electrode is less (figure 17.2).

The equilibrium reaction is shown like this:



Figure 17.2: Zinc loses electrons to form positive ions in solution. The electrons accumulate on the metal surface.

$$Cu^{2+}(aq) + 2e^{-} \Leftrightarrow Cu(s)$$

The equation lies far to the right because most of the copper is present as copper metal rather than as Cu^{2+} ions. In this half reaction, the Cu^{2+} ions are *reduced*.

17.4.3 Measuring electrode potential

If we put the two half cells together, a potential difference is set up in two places in the Zn-Cu cell:

- 1. There is a potential difference between the metal and the solution surrounding it because one is more negative than the other.
- 2. There is a potential difference between the Zn and Cu electrodes because one is more negative than the other.

It is the **potential difference** (recorded as a voltage) between the two electrodes that causes electrons, and therefore current, to flow from the more negative electrode to the less negative electrode.

The problem though is that we cannot measure the potential difference (voltage) between a metal and its surrounding solution in the cell. To do this, we would need to connect a voltmeter to both the metal and the solution, which is not possible. This means we cannot measure the exact **electrode potential** ($E^{o}V$) of a particular metal. The electrode potential describes the ability of a metal to give up electrons. And if the exact electrode potential of each of the electrodes involved can't be measured, then it is difficult to calculate the potential difference between them. But what we *can* do is to try to describe the electrode potential of a metal relative to another substance. We need to use a **standard reference electrode** for this.

17.4.4 The standard hydrogen electrode

Before we look at the standard hydrogen electrode, it may be useful to have some more understanding of the ideas behind a 'reference electrode'. Refer to the Tip box on 'Understanding the ideas behind a reference electrode' before you read further.



Important: Understanding the ideas behind a reference electrode

Adapted from www.chemguide.co.uk

Let's say that you have a device that you can use to measure heights from some distance away. You want to use this to find out how tall a particular person is. Unfortunately, you can't see their feet because they are standing in long grass. Although you can't measure their absolute height, what you can do is to measure their height relative to the post next to them. Let's say that person A for example is 15 cm *shorter* than the height of the post. You could repeat this for a number of other people (B and C). Person B is 30 cm shorter than the post and person C is 10 cm *taller* than the post.



You could summarise your findings as follows:

Person	Height relative to post (cm)	
A	-15	
В	-30	
С	+10	

Although you don't know any of their absolute heights, you can rank them in order, and do some very simple sums to work out exactly how much taller one is than another. For example, person C is 25 cm taller than A and 40 cm taller than B.

As mentioned earlier, it is difficult to measure the *absolute* electrode potential of a particular substance, but we can use a reference electrode (similar to the 'post' in the Tip box example) that we use to calculate *relative* electrode potentials for these substances. The reference electrode that is used is the **standard hydrogen electrode** (figure 17.3).

Definition: Standard hydrogen electrode

The standard hydrogen electrode is a redox electrode which forms the basis of the scale of oxidation-reduction potentials. The actual electrode potential of the hydrogen electrode is estimated to be 4.44 0.02 V at 25^{0} C, but its standard electrode potential is said to be zero at all temperatures so that it can be used as for comparison with other electrodes. The hydrogen electrode is based on the following redox half cell:

 $2H^+(aq) + 2e^- \rightarrow H_2(g)$

A standard hydrogen electrode consists of a platinum electrode in a solution containing H⁺ ions. The solution (e.g. H_2SO_4) that contains the H⁺ ions has a concentration of 1 mol.dm⁻³. As the hydrogen gas bubbles over the platinum electrode, an equilibrium is set up between hydrogen molecules and hydrogen ions in solution. The reaction is as follows:



Figure 17.3: The standard hydrogen electrode

$$2H^+(aq) + 2e^- \Leftrightarrow H_2(g)$$

The position of this equilibrium can change if you change some of the conditions (e.g. concentration, temperature). It is therefore important that the conditions for the standard hydrogen electrode are standardised as follows: pressure = 100 kPa (1atm); temperature = 298 K (25° C) and concentration = 1 mol.dm⁻³.

In order to *use* the hydrogen electrode, it needs to be attached to the electrode system that you are investigating. For example, if you are trying to determine the electrode potential of copper, you will need to connect the copper half cell to the hydrogen electrode; if you are trying to determine the electrode potential of zinc, you will need to connect the zinc half cell to the hydrogen electrode and so on. Let's look at the examples of zinc and copper in more detail.

1. **Zinc**

Zinc has a greater tendency than hydrogen to form ions, so if the standard hydrogen electrode is connected to the zinc half cell, the zinc will be relatively more negative because the electrons that are released when zinc is oxidised will accumulate on the metal. The equilibria on the two electrodes are as follows:

$$Zn^{2+}(aq) + 2e^{-} \Leftrightarrow Zn(s)$$
$$2H^{+}(aq) + 2e^{-} \Leftrightarrow H_2(g)$$

In the zinc half-reaction, the equilibrium lies far to the left and in the hydrogen half-reaction, the equilibrium lies far to the right. A simplified representation of the cell is shown in figure 17.4.

The voltmeter measures the potential difference between the charge on these electrodes. In this case, the voltmeter would read 0.76 and would show that Zn is the negative electrode (i.e. it has a relatively higher number of electrons).

2. Copper

Copper has a lower tendency than hydrogen to form ions, so if the standard hydrogen electrode is connected to the copper half cell, the hydrogen will be relatively more negative. The equilibria on the two electrodes are as follows:



Figure 17.4: When zinc is connected to the standard hydrogen electrode, relatively few electrons build up on the platinum (hydrogen) electrode. There are lots of electrons on the zinc electrode.

$$Cu^{2+}(aq) + 2e^{-} \Leftrightarrow Cu(s)$$

$$2H^{+}(aq) + 2e^{-} \Leftrightarrow H_{2}(g)$$

In the copper half-reaction, the equilibrium lies far to the right and in the hydrogen halfreaction, the equilibrium lies far to the left. A simplified representation of the cell is shown in figure 17.5.



Figure 17.5: When copper is connected to the standard hydrogen electrode, relatively few electrons build up on the copper electrode. There are lots of electrons on the hydrogen electrode.

The voltmeter measures the potential difference between the charge on these electrodes. In this case, the voltmeter would read 0.34 and would show that Cu is the positive electrode (i.e. it has a relatively lower number of electrons).

17.4.5 Standard electrode potentials

The voltages recorded earlier when zinc and copper were connected to a standard hydrogen electrode are in fact the **standard electrode potentials** for these two metals. It is important to remember that these are not *absolute* values, but are potentials that have been measured *relative* to the potential of hydrogen if the standard hydrogen electrode is taken to be zero.



Important: Conventions and voltage sign

By convention, the hydrogen electrode is written on the *left hand side* of the cell. The sign of the voltage tells you the sign of the metal electrode.

In the examples we used earlier, zinc's electrode potential is actually -0.76 and copper is +0.34. So, if a metal has a *negative* standard electrode potential, it means it forms ions easily. The more negative the value, the easier it is for that metal to form ions. If a metal has a *positive* standard electrode potential, it means it does not form ions easily. This will be explained in more detail below.

Luckily for us, we do not have to calculate the standard electrode potential for every metal. This has been done already and the results are recorded in a table of standard electrode potentials (table 17.2).

A few examples from the table are shown in table 17.3. These will be used to explain some of the trends in the table of electrode potentials.

Refer to table 17.3 and notice the following trends:

- Metals at the top of series (e.g. Li) have more negative values. This means they ionise easily, in other words, they release electrons easily. These metals are easily **oxidised** and are therefore good **reducing agents**.
- Metal ions at the bottom of the table are good at picking up electrons. They are easily **reduced** and are therefore good **oxidising agents**.
- The reducing ability (i.e. the ability to act as a reducing agent) of the metals in the table *increases* as you move *up* in the table.
- The oxidising ability of metals *increases* as you move *down* in the table.



Worked Example 84: Using the table of Standard Electrode Potentials

Question:

The following half-reactions take place in an electrochemical cell: $\begin{array}{l} Cu^{2+}+2e^-\Leftrightarrow Cu\\ Ag^-+e^-\Leftrightarrow Ag \end{array}$

- 1. Which of these reactions will be the oxidation half-reaction in the cell?
- 2. Which of these reactions will be the reduction half-reaction in the cell?

Answer

Step 5 : Determine the electrode potential for each metal

From the table of standard electrode potentials, the electrode potential for the copper half-reaction is +0.34 V. The electrode potential for the silver half-reaction is +0.80 V.

Step 6 : Use the electrode potential values to determine which metal is oxidised and which is reduced

Both values are positive, but silver has a higher positive electrode potential than copper. This means that silver does not form ions easily, in other words, silver is more likely to be *reduced*. Copper is more likely to be *oxidised* and to form ions more easily than silver. Copper is the oxidation half-reaction and silver is the reduction half-reaction.

Half-Reaction	E^0V
$Li^+ + e^- \rightleftharpoons Li$	-3.04
$K^+ + e^- \rightleftharpoons K$	-2.92
$Ba^{2+} + 2e^{-} \rightleftharpoons Ba$	-2.90
$Ca^{2+} + 2e^{-} \rightleftharpoons Ca$	-2.87
$Na^+ + e^- \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$	-2.37
$Mn^{2+} + 2e^{-} \rightleftharpoons Mn$	-1.18
$2H2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$	-0.83
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Cr^{2+} + 2e^{-} \rightleftharpoons Cr$	-0.74
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Cr^{3+} + 3e^{-} \rightleftharpoons Cr$	-0.41
$Cd^{2+} + 2e^{-} \rightleftharpoons Cd$	-0.40
$Co^{2+} + 2e^{-} \rightleftharpoons Co$	-0.28
$Ni^{2+} + 2e^{-} \rightleftharpoons Ni$	-0.25
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	-0.14
$Pb^{2+} + 2e^{-} \rightleftharpoons Pb$	-0.13
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.00
$S + 2H^+ + 2e^- \rightleftharpoons H_2S(g)$	0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	0.15
$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$	0.16
$SO_4^{2+} + 4H^+ + 2e^- \rightleftharpoons SO_2(g) + 2H_2O$	0.17
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	0.34
$2H_2O + O_2 + 4e^- \rightleftharpoons 4OH^-$	0.40
$Cu^+ + e^- \rightleftharpoons Cu$	0.52
$I_2 + 2e^- \rightleftharpoons 2I^-$	0.54
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	0.68
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	0.77
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2(g) + H_2O$	0.78
$Hg^{2+} + 2e^{-} \rightleftharpoons Hg(l)$	0.78
$Ag^+ + e^- \rightleftharpoons Ag$	0.80
$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO(g) + 2H_2O$	0.96
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.06
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	1.28
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	1.33
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.36
$Au^{3+} + 3e^- \rightleftharpoons Au$	1.50
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.52
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	1.82
$F_2 + 2e^- \rightleftharpoons 2F^-$	2.87

Table 17.2: Standard Electrode Potentials

Half-Reaction	E^0V
$Li^+ + e^- \rightleftharpoons Li$	-3.04
$Zn^{2+} + 2e^{-} \rightleftharpoons Zn$	-0.76
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	-0.04
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	0.34
$Hg^{2+} + 2e^{-} \rightleftharpoons Hg(l)$	0.78
$Ag^+ + e^- \rightleftharpoons Ag$	0.80

Table 17.3: A few examples from the table of standard electrode potentials

Important: Learning to understand the question in a problem.

Before you tackle this problem, make sure you understand exactly what the question is asking. If magnesium is able to displace silver from a solution of silver nitrate, this means that magnesium metal will form magnesium ions and the silver ions will become silver metal. In other words, there will now be *silver* metal and a solution of *magnesium nitrate*. This will only happen if magnesium has a greater tendency than silver to form ions. In other words, what the question is actually asking is whether magnesium or silver forms ions more easily.



Worked Example 85: Using the table of Standard Electrode Potentials

Question: Is magnesium able to displace silver from a solution of silver nitrate? **Answer**

Step 1 : Determine the half-reactions that would take place if magnesium were to displace silver nitrate.

The half-reactions are as follows: $Mg^{2+} + 2e^- \Leftrightarrow Mg$ $Ag^+ + e^- \Leftrightarrow Ag$

Step 2: Use the table of electrode potentials to see which metal forms ions more easily.

Looking at the electrode potentials for the magnesium and silver reactions: For the magnesium half-reaction: $E^{o}V = -2.37$ For the silver half-reaction: $E^{o}V = 0.80$

This means that magnesium is more easily **oxidised** than silver and the equilibrium in this half-reaction lies to the left. The oxidation reaction will occur spontaneously in magnesium. Silver is more easily **reduced** and the equilibrium lies to the right in this half-reaction. It can be concluded that magnesium will displace silver from a silver nitrate solution so that there is silver metal and magnesium ions in the solution.



Exercise: Table of Standard Electrode Potentials

- 1. In your own words, explain what is meant by the 'electrode potential' of a metal.
- 2. Give the standard electrode potential for each of the following metals:
 - (a) magnesium

- (b) lead
- (c) nickel
- 3. Refer to the electrode potentials in table 17.3.
 - (a) Which of the metals is most likely to be oxidised?
 - (b) Which metal is most likely to be reduced?
 - (c) Which metal is the strongest reducing agent?
 - (d) In the copper half-reaction, does the equilibrium position for the reaction lie to the left or to the right? Explain your answer.
 - (e) In the mercury half-reaction, does the equilibrium position for the reaction lie to the left or to the right? Explain your answer.
 - (f) If silver was added to a solution of copper sulphate, would it displace the copper from the copper sulphate solution? Explain your answer.
- 4. Use the table of standard electrode potentials to put the following in order from the *strongest oxidising agent* to the *weakest oxidising agent*.
 - Cu^{2+}
 - MnO₄⁻
 - Br_2
 - Zn²⁺
- 5. Look at the following half-reactions.
 - $Ca^{2+} + 2e^- \rightarrow Ca$
 - $Cl_2 + 2e^- \rightarrow 2Cl$
 - $Fe^{3+} + 3e^- \rightarrow Fe$
 - $I_2 + 2e^- \rightarrow 2I^-$
 - (a) Which substance is the strongest oxidising agent?
 - (b) Which substance is the strongest reducing agent?
- 6. Which one of the substances listed below acts as the oxidising agent in the following reaction?

$$3SO_2 + Cr_2O_7^{2-} + 2H^+ \rightarrow 3SO_4^{2-} + 2Cr^{3+} + H_2O$$

- (a) H⁺
- (b) Cr³⁺
- (c) SO_2
- (d) $Cr_2O_7^{2-}$
- (IEB Paper 2, 2004)
- 7. If zinc is added to a solution of magnesium sulphate, will the zinc displace the magnesium from the solution? Give a detailed explanation for your answer.

17.4.6 Combining half cells

Let's stay with the example of the zinc and copper half cells. If we combine these cells as we did earlier in the chapter (section 17.2), the following two equilibria exist:

$$Zn^{2+} + 2e^- \Leftrightarrow Zn(E^0 = -0.76V)$$
$$Cu^{2+} + 2e^- \Leftrightarrow Cu(E^0 = +0.34V)$$

We know from demonstrations, and also by looking at the sign of the electrode potential, that when these two half cells are combined, zinc will be the oxidation half-reaction and copper will be the reduction half-reaction. A voltmeter connected to this cell will show that the zinc electrode is more negative than the copper electrode. The reading on the meter will show the potential difference between the two half cells. This is known as the **electromotive force (emf)** of the cell.

Definition: Electromotive Force (emf)

The emf of a cell is defined as the maximum potential difference between two electrodes or half cells in a voltaic cell. emf is the electrical driving force of the cell reaction. In other words, the higher the emf, the stronger the reaction.



Definition: Standard emf (E⁰_{cell})

Standard emf is the emf of a voltaic cell operating under standard conditions (i.e. 100 kPa, concentration = 1 mol.dm⁻³ and temperature = 298 K). The symbol ⁰ denotes standard conditions.

When we want to represent this cell, it is shown as follows:

```
Zn|Zn^{2+}(1mol.dm^{-3})||Cu^{2+}(1mol.dm^{-3})|Cu|
```

The **anode** half cell (where *oxidation* takes place) is always written on the *left*. The **cathode** half cell (where *reduction* takes place) is always written on the *right*.

It is important to note that the potential difference across a cell is related to the extent to which the spontaneous cell reaction has reached equilibrium. In other words, as the reaction proceeds and the concentration of reactants decreases and the concentration of products increases, the reaction approaches equilibrium. When equilibrium is reached, the emf of the cell is zero and the cell is said to be 'flat'. There is no longer a potential difference between the two half cells, and therefore no more current will flow.

17.4.7 Uses of standard electrode potential

Standard electrode potentials have a number of different uses.

Calculating the emf of an electrochemical cell

To calculate the emf of a cell, you can use any one of the following equations:

 $E_{(cell)}^0 = E^0$ (right) - E^0 (left) ('right' refers to the electrode that is written on the right in standard cell notation. 'Left' refers to the half-reaction written on the left in this notation)

 $E^0_{(cell)} = E^0$ (reduction half reaction) - E^0 (oxidation half reaction)

 $E^0_{(cell)} = E^0$ (oxidising agent) - E^0 (reducing agent)

 $\mathsf{E}^{0}_{(cell)}=\mathsf{E}^{0}$ (cathode) - E^{0} (anode)

So, for the Zn-Cu cell,

$$E^{0}_{(cell)} = 0.34 - (-0.76)$$
$$= 0.34 + 0.76$$
$$= 1.1 \text{ V}$$



Worked Example 86: Calculating the emf of a cell

Question: The following reaction takes place:

$$Cu(s) + Ag^+(aq) \rightarrow Cu^{2+}(aq) + Ag(s)$$

- 1. Represent the cell using standard notation.
- 2. Calculate the cell potential (emf) of the electrochemical cell.

Answer

Step 1 : Write equations for the two half reactions involved $Cu^{2+} + 2e^- \Leftrightarrow Cu \ (E^{o}V = 0.16V)$ $Ag^+ + e^- \Leftrightarrow Ag \ (E^{o}V = 0.80V)$

Step 2 : Determine which reaction takes place at the cathode and which is the anode reaction $\label{eq:step2}$

Both half-reactions have positive electrode potentials, but the silver half-reaction has a higher positive value. In other words, silver does not form ions easily, and this must be the reduction half-reaction. Copper is the oxidation half-reaction. Copper is oxidised, therefore this is the anode reaction. Silver is reduced and so this is the cathode reaction.

Step 3 : Represent the cell using standard notation

 $Cu|Cu^{2+}(1mol.dm^{-3})||Ag^{+}(1mol.dm^{-3})|Ag$

Step 4 : Calculate the cell potential $E^0_{(cell)} = E^0$ (cathode) - E^0 (anode) = +0.80 - (+0.34) = +0.46 V



Worked Example 87: Calculating the emf of a cell

Question: Calculate the cell potential of the electrochemical cell in which the following reaction takes place, and represent the cell using standard notation.

$$Mg(s) + 2H^+(aq) \rightarrow Mg2 + (aq) + H_2(g)$$

Answer

Step 1 : Write equations for the two half reactions involved $Mg^{2+} + 2e^- \Leftrightarrow Mg \ (E^{o}V = -2.37)$ $2H^+ + 2e^- \Leftrightarrow H_2 \ (E^{o}V = 0.00)$

Step 2 : Determine which reaction takes place at the cathode and which is the anode reaction $\label{eq:step2}$

From the overall equation, it is clear that magnesium is oxidised and hydrogen ions are reduced in this reaction. Magnesium is therefore the anode reaction and hydrogen is the cathode reaction.

 $Step \ 3: Represent \ the \ cell \ using \ standard \ notation$

 $Mg|Mg^{2+}||H^{+}|H_{2}$

Step 4 : Calculate the cell potential $E^0_{(cell)} = E^0$ (cathode) - E^0 (anode) = 0.00 - (-2.37) = +2.37 V

Predicting whether a reaction will take place spontaneously

Look at the following example to help you to understand how to predict whether a reaction will take place spontaneously or not.

In the reaction,

$$Pb^{2+}(aq) + 2Br^{-}(aq) \rightarrow Br_2(l) + Pb(s)$$

the two half reactions are as follows:

$$Pb^{2+} + 2e^- \Leftrightarrow Pb \ (-0.13 \text{ V})$$

 $Br_2 + 2e^- \Leftrightarrow 2Br^- \ (+1.06 \text{ V})$



Important: Half cell reactions

You will see that the half reactions are written as they appear in the table of standard electrode potentials. It may be useful to highlight the reacting substance in each half reaction. In this case, the reactants are Pb^{2+} and Br^- ions.

Look at the electrode potential for the first half reaction. The negative value shows that lead loses electrons easily, in other words it is easily oxidised. The reaction would normally proceed from right to left (i.e. the equilibrium lies to the left), but in the original equation, the opposite is happening. It is the Pb^{2+} ions that are being reduced to lead. This part of the reaction is therefore not spontaneous. The positive electrode potential value for the bromine half-reaction shows that bromine is more easily reduced, in other words the equilibrium lies to the right. The spontaneous reaction proceeds from left to right. This is not what is happening in the original equation and therefore this is also not spontaneous. Overall it is clear then that the reaction will not proceed spontaneously.



Worked Example 88: Predicting whether a reaction is spontaneous

Question: Will copper react with dilute sulfuric acid (H_2SO_4) ? You are given the following half reactions:

$$Cu^{2+}(aq) + 2e^{-} \Leftrightarrow Cu(s) \ (E^{0} = +0.34 \text{ V})$$

$$2H^{+}(aq) + 2e^{-} \Leftrightarrow H_{2}(q) \ (E^{0} = 0 \text{ V})$$

Answer

Step 5 : For each reaction, look at the electrode potentials and decide in which direction the equilibrium lies

In the first half reaction, the positive electrode potential means that copper does not lose electrons easily, in other words it is more easily reduced and the equilibrium position lies to the right. Another way of saying this is that the spontaneous reaction is the one that proceeds from left to right, when copper ions are reduced to copper metal.

In the second half reaction, the spontaneous reaction is from right to left.

Step 6 : Compare the equilibrium positions to the original reaction

What you should notice is that in the original reaction, the reactants are copper (Cu) and sulfuric acid $(2H^+)$. During the reaction, the copper is oxidised and the hydrogen ions are reduced. But from an earlier step, we know that neither of these half reactions will proceed spontaneously in the direction indicated by the original reaction. The reaction is therefore not spontaneous.

Important:

A second method for predicting whether a reaction is spontaneous

Another way of predicting whether a reaction occurs spontaneously, is to look at the sign of the emf value for the cell. If the emf is **positive** then the reaction is **spontaneous**. If the emf is **negative**, then the reaction is **not spontaneous**.

Balancing redox reactions

We will look at this in more detail in the next section.



Exercise: Predicting whether a reaction will take place spontaneously

1. Predict whether the following reaction will take place spontaneously or not. Show all your working.

$$2Ag(s) + Cu^{2+}(aq) \rightarrow Cu(s) + 2Ag^{+}(aq)$$

- 2. Zinc metal reacts with an acid, H^+ (aq) to produce hydrogen gas.
 - (a) Write an equation for the reaction, using the table of electrode potentials.
 - (b) Predict whether the reaction will take place spontaneously. Show your working.
- 3. Four beakers are set up, each of which contains one of the following solutions:
 - (a) $Mg(NO_3)_2$
 - (b) Ba(NO₃)₂
 - (c) $Cu(NO_3)_2$
 - (d) $AI(NO_3)_2$

Iron is added to each of the beakers. In which beaker will a spontaneous reaction take place?

- 4. Which one of the following solutions can be stored in an aluminium container?
 - (a) $Cu(SO)_4$
 - (b) $Zn(SO)_4$
 - (c) NaCl
 - (d) $Pb(NO_3)_2$



Exercise: Electrochemical cells and standard electrode potentials

1. An electrochemical cell is made up of a copper electrode in contact with a copper nitrate solution and an electrode made of an unknown metal M in contact with a solution of MNO_3 . A salt bridge containing a KNO_3 solution joins the two half cells. A voltmeter is connected across the electrodes. Under standard conditions the reading on the voltmeter is 0.46V.



The reaction in the copper half cell is given by: $Cu \rightarrow Cu^{2+} + 2e^-$

- Ou / Ou | 20
- (a) Write down the standard conditions which apply to this electrochemical cell.
- (b) Identify the metal M. Show calculations.
- (c) Use the standard electrode potentials to write down equations for the:
 - i. cathode half-reaction
 - ii. anode half-reaction
 - iii. overall cell reaction
- (d) What is the purpose of the salt bridge?
- (e) Explain why a KCl solution would not be suitable for use in the salt bridge in this cell.

(IEB Paper 2, 2004)

(a)

2. Calculate the emf for each of the following standard electrochemical cells:

$$Mg|Mg^{2+}||H^+|H_2$$

(b)
$$Fe|Fe^{3+}||Fe^{2+}|Fe^{3+}||Fe^{2+}|Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3+}||Fe^{3$$

(c)
$$Cr|Cr2+||Cu^{2+}|Cu$$

(d)
$$Pb|Pb^{2+}||Hg^{2+}|Hg$$

- 3. Given the following two half-reactions:
 - $Fe^{3+}(aq) + e^{-} \Leftrightarrow Fe^{2+}(aq)$
 - $MnO_4^-(aq) + 8H^+(aq) + 5e^- \Leftrightarrow Mn^{2+}(aq) + 4H_2O(l)$
 - (a) Give the standard electrode potential for each half-reaction.
 - (b) Which reaction takes place at the cathode and which reaction takes place at the anode?
 - (c) Represent the electrochemical cell using standard notation.
 - (d) Calculate the emf of the cell

17.5 Balancing redox reactions

Half reactions can be used to balance redox reactions. We are going to use some worked examples to help explain the method.



Worked Example 89: Balancing redox reactions

Question: Magnesium reduces copper (II) oxide to copper. In the process, magnesium is oxidised to magnesium ions. Write a balanced equation for this reaction.

Answer

Step 1 : Write down the unbalanced oxidation half reaction.

$$Mg \rightarrow Mg^{2+}$$

Step 2 : Balance the number of atoms on both sides of the equation.

You are allowed to add hydrogen ions (H^+) and water molecules if the reaction takes place in an acid medium. If the reaction takes place in a basic medium, you can add either hydroxide ions (OH^-) or water molecules. In this case, there is one magnesium atom on the left and one on the right, so no additional atoms need to be added.

Step 3 : Once the atoms are balanced, check that the charges balance.

Charges can be balanced by adding electrons to either side. The charge on the left of the equation is 0, but the charge on the right is +2. Therefore, two electrons must be added to the right hand side so that the charges balance. The half reaction is now:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$

Step 4 : Repeat the above steps, but this time using the reduction half reaction.

The reduction half reaction is:

$$Cu^{2+} \rightarrow Cu$$

The atoms balance but the charges don't. Two electrons must be added to the right hand side.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.

No multiplication is needed because there are two electrons on either side.

Step 6 : Combine the two half reactions to get a final equation for the overall reaction.

 $Mg+Cu^{2+}+2e^-\to Mg^{2+}+Cu+2e^-$ (The electrons on either side cancel and you get...) $Mg+Cu^{2+}\to Mg^{2+}+Cu$

Step 7 : Do a final check to make sure that the equation is balanced In this case, it is.

Worked Example 90: Balancing redox reactions

Question: Chlorine gas oxidises Fe(II) ions to Fe(III) ions. In the process, chlorine is reduced to chloride ions. Write a balanced equation for this reaction.

Answer

Step 1 : Write down the oxidation half reaction.

$$Fe^{2+} \rightarrow Fe^{3+}$$

Step 2 : Balance the number of atoms on both sides of the equation.

There is one iron atom on the left and one on the right, so no additional atoms need to be added.

Step 3 : Once the atoms are balanced, check that the charges balance.

The charge on the left of the equation is +2, but the charge on the right is +3. Therefore, one electron must be added to the right hand side so that the charges balance. The half reaction is now:

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-}$$

Step 4 : Repeat the above steps, but this time using the reduction half reaction.

The reduction half reaction is:

$$Cl_2 \rightarrow Cl^-$$

The atoms don't balance, so we need to multiply the right hand side by two to fix this. Two electrons must be added to the left hand side to balance the charges.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.

We need to multiply the oxidation half reaction by two so that the number of electrons on either side are balanced. This gives:

$$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^{-}$$

Step ${\bf 6}$: Combine the two half reactions to get a final equation for the overall reaction.

$$2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$$

Step 7 : Do a final check to make sure that the equation is balanced The equation is balanced.



Worked Example 91: Balancing redox reactions in an acid medium

Question: The following reaction takes place in an acid medium:

$$Cr_2O_7^{2-} + H_2S \rightarrow Cr^{3+} + S$$

$$344$$

Write a balanced equation for this reaction.

Answer

Step 1 : Write down the oxidation half reaction.

 $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

Step 2 : Balance the number of atoms on both sides of the equation.

We need to multiply the right side by two so that the number of Cr atoms will balance. To balance the oxygen atoms, we will need to add water molecules to the right hand side.

$$Cr_2 O_7^{2-} \to 2Cr^{3+} + 7H_2 O$$

Now the oxygen atoms balance but the hydrogens don't. Because the reaction takes place in an acid medium, we can add hydrogen ions to the left side.

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

Step 3 : Once the atoms are balanced, check that the charges balance.

The charge on the left of the equation is (-2+14) = +12, but the charge on the right is +6. Therefore, six electrons must be added to the left hand side so that the charges balance. The half reaction is now:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Step 4 : Repeat the above steps, but this time using the reduction half reaction.

The reduction half reaction after the charges have been balanced is:

$$S^{2-} \rightarrow S + 2e^{-}$$

Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.

We need to multiply the reduction half reaction by three so that the number of electrons on either side are balanced. This gives:

$$3S^{2-} \rightarrow 3S + 6e^{-}$$

Step 6 : Combine the two half reactions to get a final equation for the overall reaction.

$$Cr_2 O_7^{2-} + 14H^+ + 3S^{2-} \rightarrow 3S + 2Cr^{3+} + 7H_2O_7^{3-}$$

Step 7 : Do a final check to make sure that the equation is balanced



Worked Example 92: Balancing redox reactions in an alkaline medium

Question: If ammonia solution is added to a solution that contains cobalt(II) ions, a complex ion is formed, called the hexaaminecobalt(II) ion $(Co(NH_3)_6^{2+})$. In a chemical reaction with hydrogen peroxide solution, hexaaminecobalt ions are oxidised by hydrogen peroxide solution to the hexaaminecobalt(III) ion $Co(NH_3)_6^{3+}$. Write a balanced equation for this reaction.

Answer Step 1 : Write down the oxidation half reaction

$$Co(NH_3)_6^{2+} \to Co(NH_3)_6^{3+}$$

Step 2 : Balance the number of atoms on both sides of the equation. The number of atoms are the same on both sides.

Step 3 : Once the atoms are balanced, check that the charges balance.

The charge on the left of the equation is +2, but the charge on the right is +3. One elctron must be added to the right hand side to balance the charges in the equation. The half reaction is now:

$$Co(NH_3)_6^{2+} \to Co(NH_3)_6^{3+} + e^{-}$$

Step 4 : Repeat the above steps, but this time using the reduction half reaction.

Although you don't actually know what product is formed when hydrogen peroxide is reduced, the most logical product is OH^- . The reduction half reaction is:

$$H_2O_2 \rightarrow OH^-$$

After the atoms and charges have been balanced, the final equation for the reduction half reaction is:

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

Step 5 : Multiply each half reaction by a suitable number so that the number of electrons released in the oxidation half reaction is made equal to the number of electrons that are accepted in the reduction half reaction.

We need to multiply the oxidation half reaction by two so that the number of electrons on both sides are balanced. This gives:

$$2Co(NH_3)_6^{2+} \rightarrow 2Co(NH_3)_6^{3+} + 2e^{-}$$

Step 6 : Combine the two half reactions to get a final equation for the overall reaction.

$$2Co(NH_3)_6^{2+} + H_2O_2 \rightarrow 2Co(NH_3)_6^{3+} + 2OH^{-}$$

Step 7 : Do a final check to make sure that the equation is balanced



Exercise: Balancing redox reactions

- 1. Balance the following equations.
 - (a) $HNO_3 + PbS \rightarrow PbSO_4 + NO + H_2O$
 - (b) $NaI + Fe_2(SO_4)_3 \rightarrow I_2 + FeSO_4 + Na_2SO_4$
- 2. Manganate(VII) ions (MnO_4^-) oxidise hydrogen peroxide (H₂O₂) to oxygen gas. The reaction is done in an acid medium. During the reaction, the manganate(VII) ions are reduced to manganese(II) ions (Mn²⁺). Write a balanced equation for the reaction.
- 3. Chlorine gas is prepared in the laboratory by adding concentrated hydrochloric acid to manganese dioxide powder. The mixture is carefully heated.
 - (a) Write down a balanced equation for the reaction which takes place.
 - (b) Using standard electrode potentials, show by calculations why this mixture needs to be heated.
 - (c) Besides chlorine gas which is formed during the reaction, hydrogen chloride gas is given off when the conentrated hydrochloric acid is heated. Explain why the hydrogen chloride gas is removed from the gas mixture when the gas is bubbled through water. (IEB Paper 2, 2004)
4. The following equation can be deduced from the table of standard electrode potentials:

$$2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3O_2(g) + 8H_2O(l)$$
 (E⁰ = +0.10V)

This equation implies that an acidified solution of aqueous potassium dichromate (orange) should react to form Cr^{3+} (green). Yet aqueous laboratory solutions of potassium dichromate remain orange for years. Which ONE of the following best explains this?

- (a) Laboratory solutions of aqueous potassium dichromate are not acidified
- (b) The E^0 value for this reaction is only +0.10V
- (c) The activation energy is too low
- (d) The reaction is non-spontaneous

(IEB Paper 2, 2002)

- 5. Sulfur dioxide gas can be prepared in the laboratory by heating a mixture of copper turnings and concentrated sulfuric acid in a suitable flask.
 - (a) Derive a balanced ionic equation for this reaction using the half-reactions that take place.
 - (b) Give the E^0 value for the overall reaction.
 - (c) Explain why it is necessary to heat the reaction mixture.
 - (d) The sulfur dioxide gas is now bubbled through an aqueous solution of potassium dichromate. Describe and explain what changes occur during this process.

(IEB Paper 2, 2002)

17.6 Applications of electrochemistry

Electrochemistry has a number of different uses, particularly in industry. We are going to look at a few examples.

17.6.1 Electroplating

Electroplating is the process of using electrical current to coat an electrically conductive object with a thin layer of metal. Mostly, this application is used to deposit a layer of metal that has some desired property (e.g. abrasion and wear resistance, corrosion protection, improvement of aesthetic qualities etc.) onto a surface that doesn't have that property. Electro-refining (also sometimes called *electrowinning* is electroplating on a large scale. Electrochemical reactions are used to deposit pure metals from their ores. One example is the electrorefining of copper.

Copper plays a major role in the electrical reticulation industry as it is very conductive and is used in electric cables. One of the problems though is that copper must be pure if it is to be an effective current carrier. One of the methods used to purify copper, is electro-winning. The copper electro-winning process is as follows:

- 1. Bars of crude (impure) copper containing other metallic impurities is placed on the *anodes*.
- 2. The cathodes are made up of pure copper with few impurities.
- 3. The electrolyte is a solution of aqueous $CuSO_4$ and H_2SO_4 .

4. When current passes through the cell, electrolysis takes place. The impure copper anode dissolves to form Cu²⁺ ions in solution. These positive ions are attracted to the negative cathode, where reduction takes place to produce pure copper metal. The reactions that take place are as follows:

At the anode:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$$

At the *cathode*:

 $Cu^{+2}(aq) + 2e^- \rightarrow Cu(s) \qquad (> 99\% \text{purity})$

5. The other metal impurities (Zn, Au, Ag, Fe and Pb) do not dissolve and form a solid sludge at the bottom of the tank or remain in solution in the electrolyte.



Figure 17.6: A simplified diagram to illustrate what happens during the electrowinning of copper

17.6.2 The production of chlorine

Electrolysis can also be used to produce chlorine gas from brine/seawater (NaCl). This is sometimes referred to as the 'Chlor-alkali' process. The reactions that take place are as follows:

At the *anode* the reaction is:

$$2Cl^- \rightarrow Cl_2(g) + 2e^-$$

whereas at the *cathode*, the following happens:

$$2Na^+ + 2H_2O + 2e^- \rightarrow 2Na^+ + 2OH^- + H_2$$

The overall reaction is:

$$2Na^+ + 2H_2O + 2Cl^- \rightarrow 2Na^+ + 2OH^- + H_2 + Cl_2$$

Chlorine is a very important chemical. It is used as a bleaching agent, a disinfectant, in solvents, pharmaceuticals, dyes and even plastics such as polyvinlychloride (PVC).



Figure 17.7: The electrolysis of sodium chloride

17.6.3 Extraction of aluminium

Aluminum metal is a commonly used metal in industry where its properties of being both light and strong can be utilized. It is also used in the manufacture of products such as aeroplanes and motor cars. The metal is present in deposits of bauxite which is a mixture of silicas, iron oxides and hydrated alumina $(Al_2O_3 \times H_2O)$.

Electrolysis can be used to extract aluminum from bauxite. The process described below produces 99% pure aluminum:

- 1. Aluminum is melted along with cryolite (Na_3AlF_6) which acts as the electrolyte. Cryolite helps to lower the melting point and dissolve the ore.
- 2. The anode carbon rods provide sites for the oxidation of O^{2-} and F^{-} ions. Oxygen and flourine gas are given off at the anodes and also lead to anode consumption.
- 3. At the *cathode* cell lining, the Al^{3+} ions are reduced and metal aluminum deposits on the lining.
- 4. The AlF_6^{3-} electrolyte is stable and remains in its molten state.

The basic electrolytic reactions involved are as follows: At the cathode:

$$Al^{+3} + 3e^- \rightarrow Al(s)$$
 (99% purity)

At the anode:

$$2O^{2-} \rightarrow O_2(q) + 4e -$$

The overall reaction is as follows:

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

The only problem with this process is that the reaction is *endothermic* and large amounts of electricity are needed to drive the reaction. The process is therefore very expensive.

17.7 Summary

• An **electrochemical reaction** is one where either a chemical reaction produces an external voltage, or where an external voltage causes a chemical reaction to take place.

- In a **galvanic cell** a chemical reaction produces a current in the external circuit. An example is the zinc-copper cell.
- A galvanic cell has a number of **components**. It consists of two **electrodes**, each of which is placed in a separate beaker in an **electrolyte** solution. The two electrolytes are connected by a **salt bridge**. The electrodes are connected two each other by an external circuit wire.
- One of the electrodes is the **anode**, where **oxidation** takes place. The **cathode** is the electrode where **reduction** takes place.
- In a galvanic cell, the build up of electrons at the anode sets up a potential difference between the two electrodes, and this causes a **current** to flow in the external circuit.
- A **galvanic cell** is therefore an electrochemical cell that uses a chemical reaction between two dissimilar electrodes dipped in an electrolyte to generate an electric current.
- The standard notation for a galvanic cell such as the zinc-copper cell is as follows:

$$Zn|Zn^{2+}||Cu^{2+}|Cu|$$

where

| = a phase boundary (solid/aqueous)

- || = the salt bridge
- The galvanic cell is used in **batteries** and in **electroplating**.
- An **electrolytic cell** is an electrochemical cell that uses electricity to drive a non-spontaneous reaction. In an electrolytic cell, **electrolysis** occurs, which is a process of separating elements and compounds using an electric current.
- One example of an electrolytic cell is the electrolysis of copper sulphate to produce copper and sulphate ions.
- Different metals have different **reaction potentials**. The reaction potential of metals (in other words, their ability to ionise), is recorded in a **standard table of electrode potential**. The more negative the value, the greater the tendency of the metal to be oxidised. The more positive the value, the greater the tendency of the metal to be reduced.
- The values on the standard table of electrode potentials are measured relative to the **standard hydrogen electrode**.
- The emf of a cell can be calculated using one of the following equations:

$$\mathsf{E}^{0}_{(cell)} = \mathsf{E}^{0}$$
 (right) - E^{0} (left)

- $E^0_{(cell)} = E^0$ (reduction half reaction) E^0 (oxidation half reaction)
- $E_{(cell)}^0 = E^0$ (oxidising agent) E^0 (reducing agent)

 $\mathsf{E}^{0}_{(cell)} = \mathsf{E}^{0}$ (cathode) - E^{0} (anode)

- It is possible to predict whether a reaction is **spontaneous** or not, either by looking at the sign of the cell's emf or by comparing the electrode potentials of the two half cells.
- It is possible to **balance** redox equations using the half-reactions that take place.
- There are a number of important **applications** of electrochemistry. These include **elec-troplating**, the **production of chlorine** and the **extraction of aluminium**.

- 1. For each of the following, say whether the statement is **true** or **false**. If it is false, re-write the statement correctly.
 - (a) The anode in an electrolytic cell has a negative charge.
 - (b) The reaction $2KClO_3 \rightarrow 2KCl + 3O_2$ is an example of a redox reaction.
 - (c) Lead is a stronger oxidising agent than nickel.
- 2. For each of the following questions, choose the **one correct** answer.
 - (a) Which one of the following reactions is a redox reaction?
 - i. $HCl + NaOH \rightarrow NaCl + H_2O$
 - ii. $AgNO_3 + NaI \rightarrow AgI + NaNO_3$
 - iii. $2FeCl_3 + 2H_2O + SO_2 \rightarrow H_2SO_4 + 2HCl + 2FeCl_2$
 - iv. $BaCl_2 + MgSO_4 \rightarrow MgCl_2 + BaSO_4$

(IEB Paper 2, 2003)

(b) Consider the reaction represented by the following equation:

 $Br_{2(l)} + 2I_{aq}^{-} \rightarrow 2Br_{aq}^{-} + I_{2(s)}$

Which one of the following statements about this reaction is correct?

- i. bromine is oxidised
- ii. bromine acts as a reducing agent
- iii. the iodide ions are oxidised
- iv. iodine acts as a reducing agent

(IEB Paper 2, 2002)

(c) The following equations represent two hypothetical half-reactions:

 $X_2 + 2e^- \Leftrightarrow 2X^- (+1.09 \text{ V})$ and

 $Y^+ + e^- \Leftrightarrow Y (-2.80 \text{ V})$

Which one of the following substances from these half-reactions has the greatest tendency to donate electrons?

- i. X⁻
- ii. X_2
- iii. Y
- iv. Y⁺
- (d) Which one of the following redox reactions will **not** occur spontaneously at room temperature?
 - i. $Mn + Cu^{2+} \rightarrow Mn^{2+} + Cu$
 - ii. $Zn + SO_4^{2-} + 4H^+ \rightarrow Zn^{2+} + SO_2 + 2H_2O$
 - iii. $Fe^{3+} + 3NO_2 + 3H_2O \rightarrow Fe + 3NO_3^- + 6H^+$
 - iv. $5H_2S + 2MnO_4^- + 6H^+ \rightarrow 5S + 2Mn^{2+} + 8H_2O$
- (e) Which statement is CORRECT for a Zn-Cu galvanic cell that operates under standard conditions?
 - i. The concentration of the ${\rm Zn}^{2+}$ ions in the zinc half-cell gradually decreases.
 - ii. The concentration of the ${\rm Cu}^{2+}$ ions in the copper half-cell gradually increases.
 - iii. Negative ions migrate from the zinc half-cell to the copper half-cell.
 - iv. The intensity of the colour of the electrolyte in the copper half-cell gradually decreases.

(DoE Exemplar Paper 2, 2008)

- 3. In order to investigate the rate at which a reaction proceeds, a learner places a beaker containing concentrated nitric acid on a sensitive balance. A few pieces of copper metal are dropped into the nitric acid.
 - (a) Use the relevant half-reactions from the table of Standard Reduction Potentials to derive the balanced nett ionic equation for the reaction that takes place in the beaker.
 - (b) What chemical property of nitric acid is illustrated by this reaction?
 - (c) List three observations that this learner would make during the investigation.

(IEB Paper 2, 2005)

4. The following reaction takes place in an electrochemical cell:

 $Cu(s) + 2AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2Ag(s)$

- (a) Give an equation for the oxidation half reaction.
- (b) Which metal is used as the anode?
- (c) Determine the emf of the cell under standard conditions.

(IEB Paper 2, 2003)

 The nickel-cadmium (NiCad) battery is small and light and is made in a sealed unit. It is used in portable appliances such as calculators and electric razors. The following two half reactions occur when electrical energy is produced by the cell.

 $\begin{array}{l} \mbox{Half reaction 1: } Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^- \\ \mbox{Half reaction 2: } NiO(OH)(s) + H_2O(l) + e^- \rightarrow Ni(OH)_2(s) + OH^-(aq) \end{array}$

- (a) Which half reaction (1 or 2) occurs at the anode? Give a reason for your answer.
- (b) Which substance is oxidised?
- (c) Derive a balanced ionic equation for the overall cell reaction for the discharging process.
- (d) Use your result above to state in which direction the cell reaction will proceed (forward or reverse) when the cell is being charged.

(IEB Paper 2, 2001)

6. An electrochemical cell is constructed by placing a lead rod in a porous pot containing a solution of lead nitrate (see sketch). The porous pot is then placed in a large aluminium container filled with a solution of aluminium sulphate. The lead rod is then connected to the aluminium container by a copper wire and voltmeter as shown.



- (a) Define the term *reduction*.
- (b) In which direction do electrons flow in the copper wire? (Al to Pb or Pb to Al)
- (c) Write balanced equations for the reactions that take place at...
 - i. the anode
 - ii. the cathode
- (d) Write a balanced nett ionic equation for the reaction which takes place in this cell.
- (e) What are the two functions of the porous pot?
- (f) Calculate the emf of this cell under standard conditions.
- (IEB Paper 2, 2005)

Part IV Chemical Systems

Chapter 18

The Water Cycle - Grade 10

18.1 Introduction

You may have heard the word 'cycle' many times before. Think for example of the word 'bicycle' or the regular 'cycle tests' that you may have at school. A cycle is a series of events that repeats itself. In the case of a bicycle, the wheel turns through a full circle before beginning the motion again, while cycle tests happen regularly, normally every week or every two weeks. Because a cycle repeats itself, it doesn't have a beginning or an end.

Our Earth is a **closed system**. This means that it can exchange *energy* with its surroundings (i.e. the rest of the solar system), but no new *matter* is brought into the system. For this reason, it is important that all the elements and molecules on Earth are recycled so that they are never completely used up. In the next two sections, we are going to take a closer look at two cycles that are very important for life on Earth. They are the **water cycle** and the **nitrogen cycle**.

18.2 The importance of water

For many people, it is so easy to take water for granted, and yet life on Earth would not exist were it not for this extraordinary compound. Not only is it believed that the first forms of life actually *started* in water, but most of the cells in living organisms contain between 70% and 95% water. Here in the cells, water acts as a solvent and helps to transport vital materials such as food and oxygen to where they are needed, and also removes waste products such as carbon dioxide and ammonia from the body. For many animals and plants, water is their home. Think for example of fish and amphibians that live either all or part of the time in rivers, dams and the oceans. In other words, if water did not exist, no life would be possible.

Apart from allowing life to exist, water also has a number of other functions. Water shapes the landscape around us by wearing away at rocks and also transports and deposits sediments on floodplains and along coastal regions. Water also plays a very important role in helping to regulate Earth's climate. We will discuss this again later in the chapter. As humans we use water in our homes, in industry, in mining, irrigation and even as a source of electricitiy in hydro-electric schemes. In fact, if we were able to view Earth from space, we would see that almost three quarters of our planet's surface is covered in water. It is because of this that Earth is sometimes called the 'Blue Planet'. Most of this water is stored in the oceans, with the rest found in ice (e.g. glaciers), groundwater (e.g. boreholes), surface water (e.g. rivers, lakes, estuaries, dams) and in the atmosphere as clouds and water vapour.



In the search for life on other planets, one of the first things that scientists look for is water. However, most planets are either too close to the sun (and therefore

too hot) for water to exist in liquid form, or they are too far away and therefore too cold. So, even if water were to be found, the conditions are unlikely to allow it to exist in a form that can support the diversity of life that we see on Earth.

18.3 The movement of water through the water cycle

The water cycle is the continuous movement of water over, above, and beneath the Earth's surface. As water moves, it changes phase between liquid (water), solid (ice) and gas (water vapour). It is powered by solar energy and, because it is a cycle, it has no beginning or end.



Definition: The Water Cycle

The water cycle is the continuous circulation of water across the Earth. The water cycle is driven by solar radiation and it includes the atmosphere, land, surface water and ground-water. As water moves through the cycle, it changes state between liquid, solid, and gas phases. The actual movement of water from one part of the cycle to another (e.g. from river to ocean) is the result of processes such as evaporation, precipitation, infiltration and runoff.

The movement of water through the water cycle is shown in figure 18.1. In the figure, each process within this cycle is numbered. Each process will be described below.

1. The source of energy

The water cycle is driven by the sun, which provides the heat energy that is needed for many of the other processes to take place.

2. Evaporation

When water on the earth's surface is heated by the sun, the average energy of the water molecules increases and some of the molecules are able to leave the liquid phase and become water vapour. This is called evaporation. Evaporation is the change of water from a liquid to a gas as it moves from the ground, or from bodies of water like the ocean, rivers and dams, into the atmosphere.

3. Transpiration

Transpiration is the evaporation of water from the aerial parts of plants, especially the leaves but also from the stems, flowers and fruits. This is another way that liquid water can enter the atmosphere as a gas.

4. Condensation

When evaporation takes place, water vapour rises in the atmosphere and cools as the altitude (height above the ground) increases. As the temperature drops, the energy of the water vapour molecules also decreases, until the molecules don't have enough energy to stay in the gas phase. At this point, condensation occurs. Condensation is the change of water from water vapour (gas) into liquid water droplets in the air. *Clouds, fog* and *mist* are all examples of condensation. A cloud is actually a collection of lots and lots of tiny water droplets. This mostly takes place in the upper atmosphere but can also take place close to the ground if there is a significant temperature change.



Have you ever tried breathing out on a very cold day? It looks as though you are breathing out smoke! The moist air that you breathe out is much warmer than the air outside your body. As this warm, moist air comes into



18.3

Figure 18.1: The water cycle

contact with the colder air outside, its temperature drops very quickly and the water vapour in the air you breathe out condenses. The 'smoke' that you see is actually formed in much the same way as clouds form in the upper atmosphere.

5. Precipitation

Precipitation occurs when water falls back to the earth's surface in the form of rain or snow. Rain will fall as soon as a cloud becomes too saturated with water droplets. Snow is similar to rain, except that it is frozen. Snow only falls if temperatures in the atmosphere are around freezing. The freeing point of water is 0° C).

6. Infiltration

If precipitation occurs, some of this water will filter into the soil and collect underground. This is called infiltration. This water may evaporate again from the soil at a later stage, or the underground water may seep into another water body.

7. Surface runoff

This refers to the many ways that water moves across the land. This includes *surface runoff* such as when water flows along a road and into a drain, or when water flows straight across the sand. It also includes *channel runoff* when water flows in rivers and streams. As it flows, the water may infiltrate into the ground, evaporate into the air, become stored in lakes or reservoirs, or be extracted for agricultural or other human uses.

Important: It is important to realise that the water cycle is all about **energy exchanges**. The sun is the original energy *source*. Energy from the sun heats the water and causes evaporation. This energy is stored in water vapour as *latent heat*. When the water vapour condenses again, the latent heat is released, and helps to drive circulation in the atmosphere. The liquid water falls to earth, and will evaporate again at a later stage. The atmospheric circulation patterns that occur because of these exchanges of heat are very important in influencing climate patterns.

Activity :: Experiment : The Water Cycle Materials:

Tile or piece of plastic (e.g. lid of ice-cream container) to make a hill slope; glass fish tank with a lid; beaker with ice cubes; lamp; water

Set up a model of the water cycle as follows:



- 1. Lean the plastic against one side so that it creates a 'hill slope' as shown in the diagram.
- Pour water into the bottom of the tank until about a quarter of the hill slope is covered.
- 3. Close the fish tank lid.
- 4. Place the beaker with ice on the lid directly above the hill slope.
- 5. Turn the lamp on and position it so that it shines over the water.
- 6. Leave the model like this for 20-30 minutes and then observe what happens. Make sure that you don't touch the lamp as it will be very hot!

Observation questions:

- 1. Which parts of the water cycle can you see taking place in the model?
- 2. Which parts of the water cycle are not represented in the model?

- 3. Can you think of how those parts that are not shown could be represented?
- 4. What is the energy source in the model? What would the energy source be in reality?
- 5. What do you think the function of the ice is in the beaker?

18.4 The microscopic structure of water

In many ways, water behaves very differently from other liquids. These properties are directly related to the microscopic structure of water, and more specifically to the *shape* of the molecule and its *polar nature*, and to the *bonds* that hold water molecules together.

18.4.1 The polar nature of water

Every water molecule is made up of one oxygen atom that is bonded to two hydrogen atoms. When atoms bond, the nucleus of each atom has an attractive force on the electrons of the other atoms. This 'pull' is stronger in some atoms than in others and is called the **electronegativity** of the atom. In a water molecule, the oxygen atom has a higher electronegativty than the hydrogen atoms and therefore attracts the electrons more strongly. The result is that the oxygen atom has a slightly negative charge and the two hydrogen atoms each have a slightly positive charge. The water molecule is said to be **polar** because the electrical charge is not evenly distributed in the molecule. One part of the molecule has a different charge to other parts. You will learn more about this in chapter 4.



(slightly positive charge)

Figure 18.2: Diagrams showing the structure of a water molecule. Each molecule is made up of two hydrogen atoms that are attached to one oxygen atom.

18.4.2 Hydrogen bonding in water molecules

In every water molecule, the forces that hold the individual atoms together are called **in-tramolecular forces**. But there are also forces *between* different water molecules. These are called **intermolecular forces** (figure 18.3). You will learn more about these at a later stage, but for now it is enough to know that in water, molecules are held together by **hydrogen bonds**. Hydrogen bonds are a much stronger type of intermolecular force than those found in many other substances, and this affects the properties of water.

If you find these terms confusing, remember that 'intra' means *within* (i.e. the forces within a molecule). An **introvert** is someone who doesn't express emotions and feelings outwardly. They tend to be quieter and keep to themselves. 'Inter' means *between* (i.e. the forces between molecules). An **international** cricket match is a match between two different countries.



Figure 18.3: Intermolecular and intramolecular forces in water. Note that the diagram on the left only shows *intermolecular* forces. The intramolecular forces are between the atoms of each water molecule.

18.5 The unique properties of water

Because of its polar nature and the strong hydrogen bonds between its molecules, water has some special properties that are quite different to those of other substances.

1. Absorption of infra-red radiation

The polar nature of the water molecule means that it is able to absorb infra-red radiation (heat) from the sun. As a result of this, the oceans and other water bodies act as heat reservoirs, and are able to help moderate the Earth's climate.

2. Specific heat



Definition: Specific heat

Specific heat is the amount of heat energy that is needed to increase the temperature of a substance by one degree.

Water has a high specific heat, meaning that a lot of energy must be absorbed by water before its temperature changes.

Activity :: Demonstration : The high specific heat of water

- (a) Pour about 100 ml of water into a glass beaker.
- (b) Place the beaker on a stand and heat it over a bunsen burner for about 2 minutes.
- (c) After this time, carefully touch the side of the beaker (Make sure you touch the glass very lightly because it will be very hot and may burn you!). Then use the end of a finger to test the temperature of the water.

What do you notice? Which of the two (glass or water) is the hottest?

You have probably observed this phenomenon if you have boiled water in a pot on the stove. The metal of the pot heats up very quickly, and can burn your fingers if you touch it, while the water may take several minutes before its temperature increases even slightly. How can we explain this in terms of hydrogen bonding? Remember that increasing the temperature of a substance means that its particles will move more quickly. However, before they can move faster, the bonds between them must be broken. In the case of water, these bonds are strong hydrogen bonds, and so a lot of energy is needed just to break these, before the particles can start moving faster.

It is the high specific heat of water and its ability to absorb infra-red radiation that allows it to regulate climate. Have you noticed how places that are closer to the sea have less extreme daily temperatures than those that are inland? During the day, the oceans heat up slowly, and so the air moving from the oceans across land is cool. Land temperatures are cooler than they would be if they were further from the sea. At night, the oceans lose the heat that they have absorbed very slowly, and so sea breezes blowing across the land are relatively warm. This means that at night, coastal regions are generally slightly warmer than areas that are further from the sea.

By contrast, places further from the sea experience higher maximum temperatures, and lower minimum temperatures. In other words, their *temperature range* is higher than that for coastal regions. The same principle also applies on a *global* scale. The large amount of water across Earth's surface helps to regulate temperatures by storing infra-red radiation (heat) from the sun, and then releasing it very slowly so that it never becomes too hot or too cold, and life is able to exist comfortably. In a similar way, water also helps to keep the temperature of the *internal* environment of living organisms relatively constant. This is very important. In humans, for example, a change in body temperature of only a few degrees can be deadly.

3. Melting point and boiling point

The melting point of water is 0^{0} C and its boiling point is 100^{0} C. This large difference between the melting and boiling point is very important because it means that water can exist as a liquid over a large range of temperatures. The three phases of water are shown in figure 18.4.

4. High heat of vaporisation



Definition: Heat of vaporisation

Heat of vaporisation is the energy that is needed to change a given quantity of a substance into a gas.

The strength of the hydrogen bonds between water molecules also means that it has a high heat of vaporisation. 'Heat of vaporisation' is the heat energy that is needed to change water from the liquid to the gas phase. Because the bonds between molecules are strong, water has to be heated to 100^{0} C before it changes phase. At this temperature, the molecules have enough energy to break the bonds that hold the molecules together. The heat of vaporisation for water is 40.65 kJ/mol. It is very lucky for life on earth that water does have a high heat of vaporisation. Can you imagine what a problem it would be if water's heat of vaporate and most of the water on earth would no longer be able to exist as a liquid!

5. Less dense solid phase

Another unusual property of water is that its solid phase (ice) is *less dense* than its liquid phase. You can observe this if you put ice into a glass of water. The ice doesn't sink to



Figure 18.4: Changes in phase of water

the bottom of the glass, but floats on top of the liquid. This phenomenon is also related to the hydrogen bonds between water molecules. While other materials contract when they solidify, water expands. The ability of ice to float as it solidifies is a very important factor in the environment. If ice sank, then eventually all ponds, lakes, and even the oceans would freeze solid as soon as temperatures dropped below freezing, making life as we know it impossible on Earth. During summer, only the upper few inches of the ocean would thaw. Instead, when a deep body of water cools, the floating ice insulates the liquid water below, preventing it from freezing and allowing life to exist under the frozen surface.



Figure 18.5: Ice cubes floating in water



Antarctica, the 'frozen continent', has one of the world's largest and deepest freshwater lakes. And this lake is hidden beneath 4 kilometres of ice! Lake Vostok is 200 km long and 50 km wide. The thick, glacial blanket of ice acts as an insulator, preventing the water from freezing.

Water is also a very good solvent, meaning that it is easy for other substances to dissolve in it. It is very seldom, in fact, that we find pure water. Most of the time, the water that we drink and use has all kinds of substances dissolved in it. It is these that make water taste different in different areas. So why, then, is it important that water is such a good solvent? We will look at just a few examples.

- Firstly, think about the animals and plants that live in aquatic environments such as rivers, dams or in the sea. All of these living organisms either need oxygen for respiration or carbon dioxide for photosynthesis, or both. How do they get these gases from the water in which they live? Oxygen and carbon dioxide are just two of the substances that dissolve easily in water, and this is how plants and animals obtain the gases that they need to survive. Instead of being available as gases in the atmosphere, they are present in solution in the surrounding water.
- Secondly, consider the fact that all plants need nitrogen to grow, and that they absorb this nitrogen from compounds such as nitrates and nitrates that are present in the soil. The question remains, however, as to how these nitrates and nitrites are able to be present in the soil at all, when most of the Earth's nitrogen is in a gaseous form in the atmosphere. Part of the answer lies in the fact that nitrogen oxides, which are formed during flashes of lightning, can be dissolved in rainwater and transported into the soil in this way, to be absorbed by plants. The other part of the answer lies in the activities of nitrogen-fixing bacteria in the soil, but this is a topic that we will return to in a later section.

It should be clear now, that water is an amazing compound, and that without its unique properties, life on Earth would definitely not be possible.

Exercise: The properties of water

- 1. A learner returns home from school on a hot afternoon. In order to get cold water to drink, she adds ice cubes to a glass of water. She makes the following observations:
 - The ice cubes float in the water.
 - After a while the water becomes cold and the ice cubes melt.
 - (a) What property of ice cubes allows them to float in the water?
 - (b) Briefly explain why the water gets cold when the ice cubes melt.
 - (c) Briefly describe how the property you mentioned earlier affects the survival of aquatic life during winter.
- 2. Which properties of water allow it to remain in its liquid phase over a large temperature range? Explain why this is important for life on earth.

18.6 Water conservation

Water is a very precious substance and yet far too often, earth's water resources are abused and taken for granted. How many times have you walked past polluted rivers and streams, or seen the flow of water in a river reduced to almost nothing because of its extraction for industrial and other uses? And if you were able to test the *quality* of the water you see, you would probably be shocked. Often our water resources are contaminated with chemicals such as pesticides and fertilisers. If water is to continue playing all the important functions that were discussed earlier, it is vital that we reduce the impact of humans on these resources.

?

Activity :: Group work : Human impacts on the water cycle

Read the following extract from an article, entitled 'The Effects of Urbanisation on the Water Cycle' by Susan Donaldson, and then answer the questions that follow.

As our communities grow, we notice many visible changes including housing developments, road networks, expansion of services and more. These changes have an impact on our precious water resources, with *pollution* of water being one of many such impacts. To understand these impacts you will need to have a good knowledge of the water cycle!

It is interesting to note that the oceans contain most of earth's water (about 97%). Of the freshwater supplies on earth, 78% is tied up in polar ice caps and snow, leaving only a very small fraction available for use by humans. Of the available fresh water, 98% is present as groundwater, while the remaining 2% is in the form of surface water. Because our usable water supply is so limited, it is vitally important to protect water *quality*. Within the water cycle, there is no 'new' water ever produced on the earth. The water we use today has been in existence for billions of years. The water cycle continually renews and refreshes this finite water supply.

So how exactly does urbanisation affect the water cycle? The increase in hard surfaces (e.g. roads, roofs, parking lots) decreases the amount of water that can soak into the ground. This increases the amount of surface runoff. The runoff water will collect many of the pollutants that have accumulated on these surfaces (e.g. oil from cars) and carry them into other water bodies such as rivers or the ocean. Because there is less infiltration, peak flows of stormwater runoff are larger and arrive earlier, increasing the size of urban floods. If groundwater supplies are reduced enough, this may affect stream flows during dry weather periods because it is the groundwater that seeps to the surface at these times.

Atmospheric pollution can also have an impact because condensing water vapour will pick up these pollutants (e.g. SO_2 , CO_2 and NO_2) and return them to earth into other water bodies. However, while the effects of urbanisation on water quality can be major, these impacts can be reduced if wise decisions are made during the process of development.

Questions

- 1. In groups, try to explain...
 - (a) what is meant by 'urbanisation'
 - (b) how urbanisation can affect water quality
- 2. Explain why it is so important to preserve the quality of our water supplies.
- 3. The article gives some examples of human impacts on water quality. In what *other* ways do human activities affect water quality?
- 4. What do you think some of the *consequences* of these impacts might be for humans and other forms of life?
- 5. Imagine that you are the city manager in your own city or the city closest to you. What changes would you introduce to try to protect the quality of water resources in your urban area?
- 6. What measures could be introduced in rural areas to protect water quality?

Apart from the *pollution* of water resources, the *overuse* of water is also a problem. In looking at the water cycle, it is easy sometimes to think that water is a never-ending resource. In a sense this is true because water cannot be destroyed. However, the *availability* of water may vary from place to place. In South Africa for example, many regions are extremely dry and receive very little rainfall. The same is true for many other parts of the world, where the scarcity of water

is a life and death issue. The present threat of **global warming** is also likely to affect water resources. Some climate models suggest that rising temperatures could increase the variability of climate and decrease rainfall in South Africa. With this in mind, and remembering that South Africa is already a dry country, it is vitally important that we manage our water use carefully. In addition to this, the less water there is available, the more likely it is that water *quality* will also decrease. A decrease in water quality limits how water can be used and developed.

At present, the demands being placed on South Africa's water resources are large. Table 18.1 shows the water requirements that were predicted for the year 2000. The figures in the table were taken from South Africa's *National Water Resource Strategy*, produced by the Department of Water Affairs and Forestry in 2004. In the table, 'rural' means water for domestic use and stock watering in rural areas, while 'urban' means water for domestic, industrial and commercial use in the urban area. 'Afforestation' is included because many plantations reduce stream flow because of the large amounts of water they need to survive.

Table 18.1: The predicted water requirements for various water management areas in South Africa for 2000 (million $m^3/annum$)

Water management	Irrigation	Urban	Rural	Mining	Power	Afforestatio	n Total
area				and bulk	gener-		
				industrial	ation		
Limpopo	238	34	28	14	7	1	322
Thukela	204	52	31	46	1	0	334
Upper Vaal	114	635	43	173	80	0	1045
Upper Orange	780	126	60	2	0	0	968
Breede	577	39	11	0	0	6	633
Country total	7920	2897	574	755	297	428	12871

Activity :: Case Study : South Africa's water requirements

Refer to table 18.1 and then answer the following questions:

- 1. Which water management area in South Africa has the highest need for water...
 - (a) in the mining and industry sector?
 - (b) for *power generation*?
 - (c) in the *irrigation* sector?
 - (d) Suggest reasons for each of your answers above.
- 2. For South Africa as a whole...
 - (a) Which activity uses the most water?
 - (b) Which activity uses the *least* water?
- 3. Complete the following table, by calculating the percentage (%) that each activity contributes to the total water requirements in South Africa for the year 2000.

Water use activity	% of SA's total water requirements
Irrigation	
Urban	
Rural	
Mining and bulk industry	
Power generation	
Afforestation	

Water management	Surface	Ground	Irrigatio	n Urban	Mining	Total lo-
area	water				and	cal yield
					bulk	
					indus-	
					trial	
Limpopo	160	98	8	15	0	281
Thukela	666	15	23	24	9	737
Upper Vaal	598	32	11	343	146	1130
Upper Orange	4311	65	34	37	0	4447
Breede	687	109	54	16	0	866
Country total	10240	1088	675	970	254	13227

Table 18.2: The available water yield in South Africa in 2000 for various water management areas (million $m^3/annum$)

Now look at table 18.2, which shows the amount of water *available* in South Africa during 2000. In the table, 'usable return flow' means the amount of water that can be reused after it has been used for irrigation, urban or mining.

Activity :: Case Study : Water conservation

Refer to table 18.2 and then answer the following questions:

- 1. Explain what is meant by...
 - (a) surface water
 - (b) ground water
- 2. Which water management area has the...
 - (a) lowest surface water yield?
 - (b) highest surface water yield?
 - (c) lowest *total* yield?
 - (d) highest total yield?
- 3. Look at the country's *total water requirements* for 2000 and the *total available yield*.
 - (a) Calculate what percentage of the country's water yield is already being used up.
 - (b) Do you think that the country's total water requirements will increase or decrease in the coming years? Give a reason for your answer.
- 4. South Africa is already placing a huge strain on existing water resources. In groups of 3-4, discuss ways that the country's demand for water could be reduced. Present your ideas to the rest of the class for discussion.

18.7 Summary

- Water is critical for the survival of life on Earth. It is an important part of the cells of living organisms and is used by humans in homes, industry, mining and agriculture.
- Water moves between the land and sky in the **water cycle**. The water cycle describes the changes in phase that take place in water as it circulates across the Earth. The water cycle is driven by solar radiation.

- Some of the important processes that form part of the water cycle are evaporation, transpiration, condensation, precipitation, infiltration and surface runoff. Together these processes ensure that water is cycled between the land and sky.
- It is the microscopic structure of water that determines its unique properties.
- Water molecules are **polar** and are held together by **hydrogen bonds**. These characteristics affect the properties of water.
- Some of the unique properties of water include its ability to absorb infra-red radiation, its high specific heat, high heat of vaporisation and the fact that the solid phase of water is less dense that its liquid phase.
- These properties of water help it to sustain life on Earth by moderating climate, regulating the internal environment of living organisms and allowing liquid water to exist below ice, even if temperatures are below zero.
- Water is also a good **solvent**. This property means that it is a good transport medium in the cells of living organisms, and that it can dissolve gases and other compounds that may be needed by aquatic plants and animals.
- Human activities threaten the quality of water resources through pollution and altered runoff patterns.
- As human populations grow, there is a greater demand for water. In many areas, this demand exceeds the amount of water available for use. Managing water wisely is important in ensuring that there will always be water available both for human use, and to maintain natural ecosystems.

Exercise: Summary Exercise

- 1. Give a word or term for each of the following phrases:
 - (a) The continuous circulation of water across the earth.
 - (b) The change in phase of water from gas to liquid.
 - (c) The movement of water across a land surface.
 - (d) The temperature at which water changes from liquid to gas.
- In each of the following multiple choice questions, choose the one correct answer from the list provided.
 - (a) Many of the unique properties of water (e.g. its high specific heat and high boiling point) are due to:
 - i. strong covalent bonds between the hydrogen and oxygen atoms in each water molecule
 - ii. the equal distribution of charge in a water molecule
 - iii. strong hydrogen bonds between water molecules
 - iv. the linear arrangement of atoms in a water molecule
 - (b) Which of the following statements is **false**?
 - i. Most of the water on earth is in the oceans.
 - ii. The hardening of surfaces in urban areas results in increased surface runoff.
 - iii. Water conservation is important because water cannot be recycled.
 - iv. Irrigation is one of the largest water users in South Africa.
- 3. The sketch below shows a process that leads to rainfall in town X. The town has been relying only on rainfall for its water supply because it has no access to rivers or tap water. A group of people told the community that they will never run out of rainwater *because it will never stop raining*.



- (a) List the processes labelled P_1 and P_2 that lead to rainfall in town X.
- (b) Is this group of people correct in saying that town X will never run out of rainwater? Justify your answer using the sketch. Recently, the amount of rainwater has decreased significantly. Various reasons have been given to explain the drought. Some of the community members are blaming this group who told them that it will never stop raining.
- (c) What scientific arguments can you use to convince the community members that this group of people should not be blamed for the drought?
- (d) What possible strategies can the community leaders adopt to ensure that they have a regular supply of water.

Chapter 19

Global Cycles: The Nitrogen Cycle - Grade 10

19.1 Introduction

The earth's atmosphere is made up of about 78% nitrogen, making it the largest pool of this gas. Nitrogen is essential for many biological processes. It is in all amino acids, proteins and nucleic acids. As you will see in a later chapter, these compounds are needed to build tissues, transport substances around the body, and control what happens in living organisms. In plants, much of the nitrogen is used in chlorophyll molecules which are needed for photosynthesis and growth.

So, if nitrogen is so essential for life, how does it go from being a gas in the atmosphere to being part of living organisms such as plants and animals? The problem with nitrogen is that it is an 'inert' gas, which means that it is unavailable to living organisms in its gaseous form. This is because of the strong triple bond between its atoms that makes it difficult to break. Something needs to happen to the nitrogen gas to change it into a form that it can be used. And at some later stage, these new compounds must be converted back into nitrogen gas so that the amount of nitrogen in the atmosphere stays the same. This process of changing nitrogen into different forms is called the **nitrogen cycle** (figure 19.1).



Definition: The nitrogen cycle

The nitrogen cycle is a biogeochemical cycle that describes how nitrogen and nitrogencontaining compounds are changed in nature.

Very broadly, the nitrogen cycle is made up of the following processes:

- Nitrogen fixation The process of converting inert nitrogen gas into more useable nitrogen compounds such as ammonia.
- Nitrification The conversion of ammonia into nitrites and then into nitrates, which can be absorbed and used by plants.
- Denitrification The conversion of nitrates back into nitrogen gas in the atmosphere.

We are going to look at each of these processes in more detail.

19.2 Nitrogen fixation

Nitrogen fixation is needed to change gaseous nitrogen into forms such as ammonia that are more useful to living organisms. Some fixation occurs in lightning strikes and in industrial processes,



Figure 19.1: A simplified diagram of the nitrogen cycle

but most fixation is done by different types of bacteria living either in the soil or in parts of the plants.

1. Biological fixation

Some bacteria are able to fix nitrogen. They use an enzyme called *nitrogenase* to combine gaseous nitrogen with hydrogen to form ammonia. The bacteria then use some of this ammonia to produce their own organic compounds, while what is left of the ammonia becomes available in the soil.

Some of these bacteria are free-living, in other words they live in the soil. Others live in the root nodules of legumes (e.g. soy, peas and beans). Here they form a mutualistic relationship with the plant. The bacteria get carbohydrates (food) from the plant and, in exchange, produce ammonia which can be converted into nitrogen compounds that are essential for the survival of the plant. In nutrient-poor soils, planting lots of legumes can help to enrich the soil with nitrogen compounds.

A simplified equation for biological nitrogen fixation is:

$$N_2 + 8H^+ + 8e^- \rightarrow 2NH_3 + H_2$$

Energy is used in the process, but this is not shown in the above equation.

Another important source of ammonia in the soil is **decomposition**. When animals and plants die, the nitrogen compounds that were present in them are broken down and converted into ammonia. This process is carried out by decomposition bacteria and fungi in the soil.

2. Industrial nitrogen fixation

In the Haber-Bosch process, nitrogen (N_2) is converted together with hydrogen gas (H_2) into ammonia (NH_3) fertiliser. This is an artificial process.

3. Lightning

In the atmosphere, lightning and photons are important in the reaction between nitrogen (N_2) and oxygen (O_2) to form nitric oxide (NO) and then nitrates.



It is interesting to note that by cultivating legumes, using the Haber-Bosch process to manufacture chemical fertilisers and increasing pollution from vehicles and industry, humans have more than doubled the amount of nitrogen that would normally be changed from nitrogen gas into a biologically useful form. This has serious environmental consequences.

19.3 Nitrification

Nitrification involves two biological oxidation reactions: firstly, the oxidation of ammonia with oxygen to form nitrite (NO_2^-) and secondly the oxidation of these nitrites into nitrates.

- 1. $NH_3 + O_2 \rightarrow NO_2^- + 3H^+ + 2e^-$ (production of *nitrites*)
- 2. $NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^-$ (production of *nitrates*)

Nitrification is an important step in the nitrogen cycle in soil because it converts the ammonia (from the nitrogen fixing part of the cycle) into nitrates, which are easily absorbed by the roots of plants. This absorption of nitrates by plants is called **assimilation**. Once the nitrates have been assimilated by the plants, they become part of the plants' proteins. These plant proteins are then available to be eaten by animals. In other words, animals (including humans) obtain their own nitrogen by feeding on plants. Nitrification is performed by bacteria in the soil, called *nitrifying bacteria*.

Activity :: Case Study : Nitrates in drinking water

Read the information below and then carry out your own research to help you answer the questions that follow.

The negatively charged nitrate ion is not held onto soil particles and so can be easily washed out of the soil. This is called **leaching**. In this way, valuable nitrogen can be lost from the soil, reducing the soil's fertility. The nitrates can then accumulate in groundwater, and eventually in drinking water. There are strict regulations that control how much nitrate can be present in drinking water, because nitrates can be reduced to highly reactive nitrites by microorganisms in the gut. Nitrites are absorbed from the gut and bind to haemoglobin (the pigment in blood that helps to transport oxygen around the body). This reduces the ability of the haemoglobin to carry oxygen. In young babies this can lead to respiratory distress, a condition known as "blue baby syndrome".

- 1. How is nitrate concentration in water measured?
- What concentration of nitrates in drinking water is considered acceptable? You
 can use drinking water standards for any part of the world, if you can't find any
 for South Africa.
- 3. What is 'blue baby syndrome' and what are the symptoms of the disease?

19.4 Denitrification

Denitrification is the process of reducing nitrate and nitrite into gaseous nitrogen. The process is carried out by *denitrification bacteria*. The nitrogen that is produced is returned to the atmosphere to complete the nitrogen cycle.

The equation for the reaction is:

 $2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O$

19.5 Human Influences on the Nitrogen Cycle

Humans have contributed significantly to the nitrogen cycle in a number of ways.

• Both artificial fertilisation and the planting of nitrogen fixing crops, increase the amount of nitrogen in the soil. In some ways this has positive effects because it increases the fertility of the soil, and means that agricultural productivity is high. On the other hand, however, if there is too much nitrogen in the soil, it can run off into nearby water courses such as rivers, or can become part of the groundwater supply as we mentioned earlier. Increased nitrogen in rivers and dams can lead to a problem called eutrophication. Eutrophication is a process where water bodies such as rivers, estuaries, dams and slow-moving streams receive excess nutrients (e.g. nitrogen and phosphorus compounds) that stimulate excessive plant growth. Sometimes this can cause certain plant species to be favoured over the others and one species may 'take over' the ecosystem, resulting in a decrease in plant diversity. This is called a 'bloom'. Eutrophication also affects water quality. When the plants die and decompose, large amounts of oxygen are used up and this can cause other animals in the water to die.

Activity :: Case Study : Fertiliser use in South Africa

Refer to the data table below, which shows the average fertiliser use (in kilograms per hectare or kg/ha) over a number of years for South Africa and the world. Then answer the questions that follow:

	1965	1970	1975	1980	1985	1990	1995	2000	2002
SA	27.9	42.2	57.7	80.3	66.6	54.9	48.5	47.1	61.4
World	34.0	48.9	63.9	80.6	86.7	90.9	84.9	88.2	91.9

- 1. On the same set of axes, draw two line graphs to show how fertiliser use has changed in SA and the world between 1965 and 2002.
- 2. Describe the trend you see for...
 - (a) the world
 - (b) South Africa
- 3. Suggest a reason why the world's fertiliser use has changed in this way over time.
- 4. Do you see the same pattern for South Africa?
- 5. Try to suggest a reason for the differences you see in the fertiliser use data for South Africa.
- 6. One of the problems with increased fertiliser use is that there is a greater chance of nutrient runoff into rivers and dams, and therefore a greater danger of eutrophication. In groups of 5-6, discuss the following questions:
 - (a) What could farmers do to try to reduce the risk of nutrient runoff from fields into water systems? Try to think of at least 3 different strategies that they could use.

- (b) Imagine you are going to give a presentation on eutrophication to a group of farmers who know nothing about it. How will you educate them about the dangers? How will you convince them that it is in their interests to change their farming practices? Present your ideas to the class.
- Atmospheric pollution is another problem. The main culprits are nitrous oxide (N₂O), nitric oxide (NO) and nitrogen dioxide (NO₂). Most of these gases result either from emissions from agricultural soils (and particularly artificial fertilisers), or from the combustion of fossil fuels in industry or motor vehicles. The combustion (burning) of nitrogen-bearing fuels such as coal and oil releases this nitrogen as N₂ or NO gases. Both NO₂ and NO can combine with water droplets in the atmosphere to form acid rain. Furthermore, both NO and NO₂ contribute to the depletion of the ozone layer and some are greenhouse gases. In high concentrations these gases can contribute towards global warming.

19.6 The industrial fixation of nitrogen

A number of industrial processes are able to fix nitrogen into different compounds and then convert these compounds into fertilisers. In the descriptions below, you will see how atmospheric nitrogen is fixed to produce ammonia, how ammonia is then reacted with oxygen to form nitric acid and how nitric acid and ammonia are then used to produce the fertiliser, ammonium nitrate.

• Preparation of ammonia (NH₃)

The industrial preparation of ammonia is known as the **Haber-Bosch process**. At a high pressure and a temperature of approximately 500⁰C, and in the presence of a suitable catalyst (usually iron), nitrogen and hydrogen react according to the following equation:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Ammonia is used in the preparation of artificial fertilisers such as $(NH_4)_2SO_4$ and is also used in cleaning agents and cooling installations.



Fritz Haber and Carl Bosch were the two men responsible for developing the Haber-Bosch process. In 1918, Haber was awarded the Nobel Prize in Chemistry for his work. The Haber-Bosch process was a milestone in industrial chemistry because it meant that nitrogenous fertilisers were cheaper and much more easily available. At the time, this was very important in providing food for the growing human population.

Haber also played a major role in the development of chemical warfare in World War I. Part of this work included the development of gas masks with absorbent filters. He also led the teams that developed chlorine gas and other deadly gases for use in trench warfare. His wife, Clara Immerwahr, also a chemist, opposed his work on poison gas and committed suicide with his service weapon in their garden. During the 1920s, scientists working at his institute also developed the cyanide gas formulation Zyklon B, which was used as an insecticide and also later, after he left the programme, in the Nazi extermination camps.

Haber was Jewish by birth, but converted from Judaism in order to be more accepted in Germany. Despite this, he was forced to leave the country in 1933 because he was Jewish 'by definition' (his mother was Jewish). He died in 1934 at the age of 65. Many members of his extended family died in the Nazi concentration camps, possibly gassed by Zyklon B.

• Preparation of nitric acid (HNO₃)

Nitric acid is used to prepare fertilisers and explosives. The industrial preparation of nitric acid is known as the **Ostwald process**. The Ostwald process involves the conversion of ammonia into nitric acid in various stages:

Firstly, ammonia is heated with oxygen in the presence of a platinum catalyst to form nitric oxide and water.

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

Secondly, nitric oxide reacts with oxygen to form nitrogen dioxide. This gas is then readily absorbed by the water to produce nitric acid. A portion of nitrogen dioxide is reduced back to nitric oxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

The NO is recycled, and the acid is concentrated to the required strength by a process called *distillation*.

• Preparation of ammonium nitrate

Ammonium nitrate is used as a fertiliser, as an explosive and also in the preparation of 'laughing gas' which is used as an anaesthetic. Ammonium nitrate is prepared by reacting ammonia with nitric acid:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Activity :: Debate : Fertiliser use

Divide the class into two groups to debate the following topic:

Increasing the use of artificial fertilisers is the best solution to meet the growing food needs of the world's human population.

One group should take the position of *agreeing* with the statement, and the other should *disagree*. In your groups, discuss reasons why you have the opinion that you do, and record some notes of your discussion. Your teacher will then explain to you how to proceed with the debate.

19.7 Summary

- Nitrogen is essential for life on earth, since it forms part of amino acids, proteins and nucleic acids.
- The **atmosphere** is composed mostly of nitrogen gas, but the gas is **inert**, meaning that it is not available to living organisms in its gaseous form.
- The **nitrogen cycle** describes how nitrogen and nitrogen-containing compounds are changed into different forms in nature.

- The nitrogen cycle consists of three major processes: **nitrogen fixation**, **nitrification** and **denitrification**.
- **Nitrogen fixation** is the conversion of atmospheric nitrogen into compounds such as ammonia, that are more easily used.
- Nitrogen can be fixed **biologically** through the actions of **bacteria**, **industrially** through the **Haber-Bosch process** or by **lightning**.
- Nitrification converts ammonia into nitrites and nitrates, which can be easily assimilated by plants.
- **Denitrification** converts nitrites and nitrates back into gaseous nitrogen to complete the nitrogen cycle.
- Humans have had a number of impacts on the nitrogen cycle. The production of artificial fertilisers for example, means that there is a greater chance of runoff into water systems. In some cases, eutrophication may occur.
- **Eutrophication** is the enrichment of water systems with excess nutrients, which may stimulate excessive plant growth at the expense of other parts of the ecosystem.
- Many nitrogen gases such as NO, N₂O and NO₂ are released by agricultural soils and artificial fertilisers. These gases may combine with water vapour in the atmosphere and result in **acid rain**. Some of these gases are also greenhouse gases and may contribute towards **global warming**.
- A number of industrial processes are used to produce articifical fertilisers.
- The Haber-Bosch process converts atmsopheric nitrogen into ammonia.
- The **Ostwald process** reacts ammonia with oxygen to produce **nitric acid**, which is used in the preparation of fertilisers and explosives.
- If ammonia and nitric acid react, the product is **ammonium nitrate**, which is used as a fertiliser and as an explosive.



Exercise: Summary Exercise

- 1. Look at the diagram and the descriptions of the nitrogen cycle earlier in the chapter:
 - (a) Would you describe the changes that take place in the nitrogen cycle as *chemical* or *physical* changes? Explain your answer.
 - (b) Are the changes that take place in the water cycle *physical* or *chemical* changes? Explain your answer.
- 2. Explain what is meant by each of the following terms:
 - (a) nitrogen fixing
 - (b) fertiliser
 - (c) eutrophication
- 3. Explain why the fixing of atmospheric nitrogen is so important for the survival of life on earth.
- 4. Refer to the diagram below and then answer the questions that follow:



- (a) Explain the role of *decomposers* in the nitrogen cycle.
- (b) If the process taking place at (3) is *nitrification*, then label the processes at (1) and (5).
- (c) Identify the nitrogen products at (2) and (4).
- (d) On the diagram, indicate the type of *bacteria* that are involved in each stage of the nitrogen cycle.
- (e) In industry, what process is used to produce the compound at 2?
- (f) Does the diagram above show a 'cycle'? Explain your answer.
- 5. NO and NO_2 are both nitrogen compounds:
 - (a) Explain how each of these compounds is formed?
 - (b) What effect does each of these compounds have in the environment?
- 6. There are a number of arguments both 'for' and 'against' the use of artificial fertilisers. Draw a table to summarise the advantages and disadvantages of their use.

Chapter 20

The Hydrosphere - Grade 10

20.1 Introduction

As far as we know, the Earth we live on is the only planet that is able to support life. Among other things, Earth is just the right distance from the sun to have temperatures that are suitable for life to exist. Also, the Earth's atmosphere has exactly the right type of gases in the right amounts for life to survive. Our planet also has **water** on its surface, which is something very unique. In fact, Earth is often called the 'Blue Planet' because most of it is covered in water. This water is made up of *freshwater* in rivers and lakes, the *saltwater* of the oceans and estuaries, *groundwater* and *water vapour*. Together, all these water bodies are called the **hydrosphere**.

20.2 Interactions of the hydrosphere

It is important to realise that the hydrosphere interacts with other global systems, including the *atmosphere*, *lithosphere* and *biosphere*.

• Atmosphere

When water is heated (e.g. by energy from the sun), it evaporates and forms water vapour. When water vapour cools again, it condenses to form liquid water which eventually returns to the surface by precipitation e.g. rain or snow. This cycle of water moving through the atmosphere, and the energy changes that accompany it, is what drives weather patterns on earth.

• Lithosphere

In the lithosphere (the ocean and continental crust at the Earth's surface), water is an important *weathering* agent, which means that it helps to break rock down into rock fragments and then soil. These fragments may then be transported by water to another place, where they are deposited. This is called *erosion*. These two process i.e. weathering and erosion, help to shape the earth's surface. You can see this for example in rivers. In the upper streams, rocks are eroded and sediments are transported down the river and deposited on the wide flood plains lower down. On a bigger scale, river valleys in mountains have been carved out by the action of water, and cliffs and caves on rocky beach coastlines, are also the result of weathering and erosion by water.

• Biosphere

In the biosphere, land plants absorb water through their roots and then transport this through their vascular (transport) system to stems and leaves. This water is needed in *photosynthesis*, the food production process in plants. Transpiration (evaporation of water from the leaf surface) then returns water back to the atmosphere.

20.3 Exploring the Hydrosphere

The large amount of water on our planet is something quite unique. In fact, about 71% of the earth is covered by water. Of this, almost 97% is found in the oceans as saltwater, about 2.2% occurs as a solid in ice sheets, while the remaining amount (less than 1%) is available as freshwater. So from a human perspective, despite the vast amount of water on the planet, only a very small amount is actually available for human consumption (e.g. drinking water). Before we go on to look more closely at the chemistry of the hydrosphere, we are going to spend some time exploring a part of the hydrosphere, in order to start appreciating what a complex and beautiful part of the world it is.

Activity :: Investigation : Investigating the hydrosphere

1. Choosing a study site:

For this exercise, you can choose any part of the hydrosphere that you would like to explore. This may be a rock pool, a lake, river, wetland or even just a small pond. The guidelines below will apply best to a river investigation, but you can ask similar questions and gather similar data in other areas. When choosing your study site, consider how accessible it is (how easy is it to get to?) and the problems you may experience (e.g. tides, rain).

2. Collecting data:

Your teacher will provide you with the equipment you need to collect the following data. You should have at least one study site where you will collect data, but you might decide to have more if you want to compare your results in different areas. This works best in a river, where you can choose sites down its length.

(a) Chemical data

Measure and record data such as temperature, pH, conductivity and dissolved oxygen at each of your sites. You may not know exactly what these measurements mean right now, but it will become clearer later in the chapter.

(b) Hydrological data

Measure the water velocity of the river and observe how the volume of water in the river changes as you move down its length. You can also collect a water sample in a clear bottle, hold it to the light and see whether the water is clear or whether it has particles in it.

(c) Biological data

What types of animals and plants are found in or near this part of the hydrosphere? Are they specially adapted to their environment?

	Site 1	Site 2	Site 3
Temperature			
pН			
Conductivity			
Dissolved oxygen			
Animals and plants			

Record your data in a table like the one shown below:

3. Interpreting the data:

Once you have collected and recorded your data, think about the following questions:

- How does the data you have collected vary at different sites?
- Can you explain these differences?
- What effect do you think *temperature*, *dissolved oxygen* and *pH* have on animals and plants that are living in the hydrosphere?

- Water is seldom 'pure'. It usually has lots of things dissolved (e.g. Mg, Ca and NO₃⁻ ions) or suspended (e.g. soil particles, debris) in it. Where do these substances come from?
- Are there any human activities near this part of the hydrosphere? What effect could these activities have on the hydrosphere?

20.4 The Importance of the Hydrosphere

It is so easy sometimes to take our hydrosphere for granted, and we seldom take the time to really think about the role that this part of the planet plays in keeping us alive. Below are just some of the very important functions of water in the hydrosphere:

• Water is a part of living cells

Each cell in a living organism is made up of almost 75% water, and this allows the cell to function normally. In fact, most of the chemical reactions that occur in life, involve substances that are dissolved in water. Without water, cells would not be able to carry out their normal functions, and life could not exist.

• Water provides a habitat

The hydrosphere provides an important place for many animals and plants to live. Many gases (e.g. CO_2 , O_2), nutrients e.g. nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) ions, as well as other ions (e.g. Ca^{2+} and Mg^{2+}) are dissolved in water. The presence of these substances is critical for life to exist in water.

• Regulating climate

You may remember from chapter **??** that one of water's unique characteristics is its high *specific heat*. This means that water takes a long time to heat up, and also a long time to cool down. This is important in helping to regulate temperatures on earth so that they stay within a range that is acceptable for life to exist. *Ocean currents* also help to disperse heat.

• Human needs

Humans use water in a number of ways. Drinking water is obviously very important, but water is also used domestically (e.g. washing and cleaning) and in industry. Water can also be used to generate electricity through hydropower.

These are just a few of the very important functions that water plays on our planet. Many of the functions of water relate to its chemistry and to the way in which it is able to dissolve substances in it.

20.5 lons in aqueous solution

As we mentioned earlier, water is seldom pure. Because of the structure of the water molecule, it is able to dissolve substances in it. This is very important because if water wasn't able to do this, life would not be able to survive. In rivers and the oceans for example, dissolved oxygen means that organisms are still able to respire (breathe). For plants, dissolved nutrients are also available. In the human body, water is able to carry dissolved substances from one part of the body to another.

Many of the substances that dissolve are *ionic*, and when they dissolve they form ions in solution. We are going to look at how water is able to dissolve ionic compounds, and how these ions maintain a balance in the human body, how they affect water hardness, and how specific ions determine the pH of solutions.

20.5.1 Dissociation in water

You may remember from chapter 5 that water is a **polar molecule** (figure 20.1). This means that one part of the molecule has a slightly positive charge and the other part has a slightly negative charge.



Figure 20.1: Water is a polar molecule

It is the polar nature of water that allows ionic compounds to dissolve in it. In the case of sodium chloride (NaCl) for example, the positive sodium ions (Na⁺) will be attracted to the negative pole of the water molecule, while the negative chloride ions (Cl⁻) will be attracted to the positive pole of the water molecule. In the process, the ionic bonds between the sodium and chloride ions are weakened and the water molecules are able to work their way between the individual ions, surrounding them and slowly dissolving the compound. This process is called **dissociation**. A simplified representation of this is shown in figure 20.2.



Definition: Dissociation

Dissociation in chemistry and biochemistry is a general process in which ionic compounds separate or split into smaller molecules or ions, usually in a reversible manner.



Figure 20.2: Sodium chloride dissolves in water

The dissolution of sodium chloride can be represented by the following equation:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

The symbols **s** (solid), **l** (liquid), **g** (gas) and **aq** (material is dissolved in water) are written after the chemical formula to show the state or phase of the material. The dissolution of potassium sulphate into potassium and sulphate ions is shown below as another example:

20.5

$$K_2SO_4(s) \to 2K^+(aq) + SO_4^{2-}(aq)$$

Remember that **molecular** substances (e.g. covalent compounds) may also dissolve, but most will not form ions. One example is sugar.

$$C_6H_{12}O_6(s) \Leftrightarrow C_6H_{12}O_6(aq)$$

There are exceptions to this and some molecular substances *will* form ions when they dissolve. Hydrogen chloride for example can ionise to form hydrogen and chloride ions.

$$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$$



The ability of ionic compounds to dissolve in water is extremely important in the human body! The body is made up of *cells*, each of which is surrounded by a membrane. Dissolved ions are found inside and outside of body cells, in different concentrations. Some of these ions are positive (e.g. Mg^{2+}) and some are negative (e.g. Cl⁻). If there is a difference in the charge that is inside and outside the cell, then there is a *potential difference* across the cell membrane. This is called the **membrane potential** of the cell. The membrane potential acts like a battery and affects the movement of all charged substances across the membrane. Membrane potentials play a role in muscle functioning, digestion, excretion and in maintaining blood pH, to name just a few. The movement of ions across the membrane can also be converted into an electric signal that can be transferred along *neurons* (nerve cells), which control body processes. If ionic substances were not able to dissociate in water, then none of these processes would be possible! It is also important to realise that our bodies can lose ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^- , for example when we sweat during exercise. Sports drinks such as Lucozade and Powerade are designed to replace these lost ions so that the body's normal functioning is not affected.



Exercise: lons in solution

- 1. For each of the following, say whether the substance is ionic or molecular.
 - (a) potassium nitrate (KNO₃)
 - (b) ethanol (C_2H_5OH)
 - (c) sucrose sugar ($C_{12}H_{22}O_{11}$
 - (d) sodium bromide (NaBr)
- 2. Write a balanced equation to show how each of the following ionic compounds dissociate in water.
 - (a) sodium sulphate (Na_2SO_4)
 - (b) potassium bromide (KBr)
 - (c) potassium permanganate (KMNO₄)
 - (d) sodium phosphate (Na₃PO₄)

20.5.2 lons and water hardness



Definition: Water hardness

Water hardness is a measure of the mineral content of water. Minerals are substances such as calcite, quartz and mica that occur naturally as a result of geological processes.

Hard water is water that has a high mineral content. Water that has a low mineral content is known as **soft water**. If water has a high mineral content, it usually contains high levels of metal ions, mainly calcium (Ca) and magnesium (Mg). The calcium enters the water from either CaCO₃ (limestone or chalk) or from mineral deposits of CaSO₄. The main source of magnesium is a sedimentary rock called dolomite, CaMg(CO₃)₂. Hard water may also contain other metals as well as bicarbonates and sulphates.



The simplest way to check whether water is hard or soft is to use the lather/froth test. If the water is very soft, soap will lather more easily when it is rubbed against the skin. With hard water this won't happen. Toothpaste will also not froth well in hard water.

A water softener works on the principle of ion exchange. Hard water passes through a media bed, usually made of resin beads that are supersaturated with sodium. As the water passes through the beads, the hardness minerals (e.g. calcium and magnesium) attach themselves to the beads. The sodium that was originally on the beads is released into the water. When the resin becomes saturated with calcium and magnesium, it must be recharged. A salt solution is passed through the resin. The sodium replaces the calcium and magnesium, and these ions are released into the waste water and discharged.

20.5.3 The pH scale

The concentration of specific ions in solution, affects whether the solution is acidic or basic. You will learn about acids and bases in chapter 15. Acids and bases can be described as substances that either increase or decrease the concentration of hydrogen (H^+ or H_3O_+) ions in a solution. An acid *increases* the hydrogen ion concentration in a solution, while a base *decreases* the hydrogen ion concentration. **pH** is used to measure whether a substance is acidic or basic (alkaline).



Definition: pH

pH is a measure of the acidity or alkalinity of a solution. The pH scale ranges from 0 to 14. Solutions with a pH less than seven are acidic, while those with a pH greater than seven are basic (alkaline). pH 7 is considered neutral.

pH can be calculated using the following equation:

$$pH = -log[H^+]$$

or

$$pH = -log[H_3O^+]$$

The brackets in the above equation are used to show *concentration* in mol.dm $^{-3}$.
Worked Example 93: pH calculations

Question: Calculate the pH of a solution where the concentration of hydrogen ions is $1\times 10^{-7}~\text{mol.dm}^{-3}.$

Answer

Step 1 : Determine the concentration of hydrogen ions in mol.dm $^{-3}$ In this example, the concentration has been given and is 1×10^{-7} mol.dm $^{-3}$

Step 2 : Substitute this value into the pH equation and calculate the pH value $pH = -log[H^+]$

 $= -\log(1 \times 10^{-7})$ = 7



Worked Example 94: pH calculations

Question: In a solution of ethanoic acid, the following equilibrium is established:

 $CH_3COOH(aq) + H_2O \Leftrightarrow CH_3COO^-(aq) + H_3O^+$

The concentration of CH_3COO^- ions is found to be 0.003 mol.dm^{-3}. Calculate the pH of the solution.

Answer

Step 1 : Determine the concentration of hydrogen ions in the solution

According to the balanced equation for this reaction, the mole ratio of CH_3COO^- ions to H_3O^+ ions is the same, therefore the concentration of these two ions in the solution will also be the same. So, $[H_3O^+] = 0.003 \text{ dm}^{-3}$.

Step 2 : Substitute this value into the pH equation and calculate the pH value

 $pH = -log[H_3O^+]$ = -log(0.003) = 2.52

Understanding pH is very important. In living organisms, it is necessary to maintain a constant pH so that chemical reactions can occur under optimal conditions.

Important: It may also be useful for calculations involving the pH scale, to know that the following equation can also be used:

 $[H_3O^+][OH^-] = 1 \times 10^{-14}$



A build up of acid in the human body can be very dangerous. Lactic acidosis is a condition caused by the buildup of lactic acid in the body. It leads to acidification of the blood (acidosis) and can make a person very ill. Some of the symptoms of lactic acidosis are deep and rapid breathing, vomiting, and abdominal pain. In the fight against HIV, lactic acidosis is a problem. One of the antiretrovirals (ARV's) that is used in anti-HIV treatment is Stavudine (also known as Zerit or d4T). One of the side effects of Stavudine is lactic acidosis, particularly in overweight women. If it is not treated quickly, it can result in death.

In agriculture, farmers need to know the pH of their soils so that they are able to plant the right kinds of crops. The pH of soils can vary depending on a number of factors such as rainwater, the kinds of rocks and materials from which the soil was formed and also human influences such as pollution and fertilisers. The pH of rain water can also vary and this too has an effect on agriculture, buildings, water courses, animals and plants. Rainwater is naturally acidic because carbon dioxide in the atmosphere combines with water to form carbonic acid. Unpolluted rainwater has a pH of approximately 5.6. However, human activities can alter the acidity of rain and this can cause serious problems such as acid rain.



Exercise: Calculating pH

- 1. Calculate the pH of each of the following solutions:
 - (a) A 0.2 mol.dm $^{-3}$ KOH solution
 - (b) A 0.5 mol.dm $^{-3}$ HCl solution
- 2. What is the concentration (in mol.dm $^{-3}$) of H₃O⁺ ions in a NaOH solution which has a pH of 12?
- 3. The concentrations of hydronium and hydroxyl ions in a typical sample of seawater are 10^{-8} mol.dm⁻³ and 10^{-6} mol.dm⁻³ respectively.
 - (a) Is the seawater acidic or basic?
 - (b) What is the pH of the seawater?
 - (c) Give a possible explanation for the pH of the seawater.
 - (IEB Paper 2, 2002)

20.5.4 Acid rain

The acidity of rainwater comes from the natural presence of three substances (CO₂, NO, and SO₂) in the lowest layer of the atmosphere. These gases are able to dissolve in water and therefore make rain more acidic than it would otherwise be. Of these gases, carbon dioxide (CO₂) has the highest concentration and therefore contributes the most to the natural acidity of rainwater. We will look at each of these gases in turn.



Definition: Acid rain

Acid rain refers to the deposition of acidic components in rain, snow and dew. Acid rain occurs when sulfur dioxide and nitrogen oxides are emitted into the atmosphere, undergo chemical transformations, and are absorbed by water droplets in clouds. The droplets then fall to earth as rain, snow, mist, dry dust, hail, or sleet. This increases the acidity of the soil, and affects the chemical balance of lakes and streams.

1. Carbon dioxide

Carbon dioxide reacts with water in the atmosphere to form carbonic acid (H_2CO_3) .

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The carbonic acid dissociates to form hydrogen and hydrogen carbonate ions. It is the presence of hydrogen ions that lowers the pH of the solution, making the rain acidic.

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

2. Nitric oxide

Nitric oxide (NO) also contributes to the natural acidity of rainwater and is formed during lightning storms when nitrogen and oxygen react. In air, NO is oxidised to form nitrogen dioxide (NO₂). It is the nitrogen dioxide which then reacts with water in the atmosphere to form **nitric acid** (HNO₃).

$$3NO_2(g) + H_2O \rightarrow 2HNO_3(aq) + NO(g)$$

The nitric acid dissociates in water to produce hydrogen ions and nitrate ions. This again lowers the pH of the solution, making it acidic.

$$HNO_3 \rightarrow H^+ + NO_3^-$$

3. Sulfur dioxide

Sulfur dioxide in the atmosphere first reacts with oxygen to form sulfur trioxide, before reacting with water to form **sulfuric acid**.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfuric acid dissociates in a similar way to the previous reactions.

$$H_2SO_4 \rightarrow HSO_4^- + H^+$$

Although these reactions do take place naturally, human activities can greatly increase the concentration of these gases in the atmosphere, so that rain becomes far more acidic than it would otherwise be. The burning of fossil fuels in industries, vehicles etc is one of the biggest culprits. If the acidity of the rain drops below 5, it is referred to as **acid rain**.

Acid rain can have a very damaging effect on the environment. In rivers, dams and lakes, increased acidity can mean that some species of animals and plants will not survive. Acid rain can also degrade soil minerals, producing metal ions that are washed into water systems. Some of these ions may be toxic e.g. Al³⁺. From an economic perspective, altered soil pH can drastically affect agricultural productivity.

Acid rain can also affect buildings and monuments, many of which are made from marble and limestone. A chemical reaction takes place between $CaCO_3$ (limestone) and sulfuric acid to produce aqueous ions which can be easily washed away. The same reaction can occur in the lithosphere where limestone rocks are present e.g. limestone caves can be eroded by acidic rainwater.

$$H_2SO_4 + CaCO_3 \rightarrow CaSO_4.H_2O + CO_2$$

Activity :: Investigation : Acid rain

You are going to test the effect of 'acid rain' on a number of substances. *Materials needed:*

samples of chalk, marble, zinc, iron, lead, dilute sulfuric acid, test tubes, beaker, glass dropper

Method:

- 1. Place a small sample of each of the following substances in a separate test tube: chalk, marble, zinc, iron and lead
- 2. To each test tube, add a few drops of dilute sulfuric acid.
- 3. Observe what happens and record your results.

Discussion questions:

- In which of the test tubes did reactions take place? What happened to the sample substances?
- What do your results tell you about the effect that acid rain could have on each of the following: buildings, soils, rocks and geology, water ecosystems?
- What precautions could be taken to reduce the potential impact of acid rain?

20.6 Electrolytes, ionisation and conductivity

Conductivity in aqueous solutions, is a measure of the ability of water to conduct an electric current. The more **ions** there are in the solution, the higher its conductivity.



Definition: Conductivity

Conductivity is a measure of a solution's ability to conduct an electric current.

20.6.1 Electrolytes

An **electrolyte** is a material that *increases* the conductivity of water when dissolved in it. Electrolytes can be further divided into **strong electrolytes** and **weak electrolytes**.



Definition: Electrolyte

An electrolyte is a substance that contains free ions and behaves as an electrically conductive medium. Because they generally consist of ions in solution, electrolytes are also known as ionic solutions.

1. Strong electrolytes

A strong electrolyte is a material that ionises completely when it is dissolved in water:

$$AB(s,l,g) \rightarrow A^+(aq) + B^-(aq)$$

This is a **chemical change** because the original compound has been split into its component ions and bonds have been broken. In a strong electrolyte, we say that the *extent of ionisation* is high. In other words, the original material dissociates completely so that there is a high concentration of ions in the solution. An example is a solution of potassium nitrate:

$$KNO_3(s) \rightarrow K^+(aq) + NO_3^-(aq)$$

2. Weak electrolytes

A weak electrolyte is a material that goes into solution and will be surrounded by water molecules when it is added to water. However, not *all* of the molecules will dissociate into ions. The *extent of ionisation* of a weak electrolyte is low and therefore the concentration of ions in the solution is also low.

$$AB(s,l,g) \to AB(aq) \Leftrightarrow A^+(aq) + B^-(aq)$$

The following example shows that, in the final solution of a weak electrolyte, some of the original compound *plus* some dissolved ions are present.

$$C_2H_3O_2H(l) \rightarrow C_2H_3O_2H \Leftrightarrow C_2H_3O_2^-(aq) + H^+(aq)$$

20.6.2 Non-electrolytes

A **non-electrolyte** is a material that does not increase the conductivity of water when dissolved in it. The substance goes into solution and becomes surrounded by water molecules, so that the molecules of the chemical become separated from each other. However, although the substance does dissolve, it is not changed in any way and no chemical bonds are broken. The change is a **physical change**. In the oxygen example below, the reaction is shown to be reversible because oxygen is only partially soluble in water and comes out of solution very easily.

$$C_2H_5OH(l) \rightarrow C_2H_5OH(aq)$$

$$O_2(g) \Leftrightarrow O_2(aq)$$

20.6.3 Factors that affect the conductivity of water

The conductivity of water is therefore affected by the following factors:

• The type of substance that dissolves in water

Whether a material is a strong electrolyte (e.g. potassium nitrate, KNO_3), a weak electrolyte (e.g. acetate, $C_2H_3O_2H$) or a non-electrolyte (e.g. sugar, alcohol, oil) will affect the conductivity of water because the concentration of ions in solution will be different in each case.

• The concentration of ions in solution

The higher the concentration of ions in solution, the higher its conductivity will be.

• Temperature

The warmer the solution the higher the solubility of the material being dissolved, and therefore the higher the conductivity as well.

Activity :: Experiment : Electrical conductivity Aim:

To investigate the electrical conductivities of different substances and solutions. **Apparatus:**

solid salt (NaCl) crystals; different liquids such as distilled water, tap water, seawater, benzene and alcohol; solutions of salts e.g. NaCl, KBr; a solution of an acid (e.g. HCl) and a solution of a base (e.g. NaOH); torch cells; ammeter; conducting wire, crocodile clips and 2 carbon rods.

Method:

Set up the experiment by connecting the circuit as shown in the diagram below. In the diagram, 'X' represents the substance or solution that you will be testing. When you are using the solid crystals, the crocodile clips can be attached directly to each end of the crystal. When you are using solutions, two carbon rods are placed into the liquid, and the clips are attached to each of the rods. In each case, complete the circuit and allow the current to flow for about 30 seconds. Observe whether the ammeter shows a reading.



Results:

Record your observations in a table similar to the one below:

Test substance	Ammeter reading

What do you notice? Can you explain these observations?

Remember that for electricity to flow, there needs to be a movement of charged particles e.g. ions. With the solid NaCl crystals, there was no flow of electricity recorded on the ammeter. Although the solid is made up of ions, they are held together very tightly within the crystal lattice, and therefore no current will flow. Distilled water, benzene and alcohol also don't conduct a current because they are *covalent compounds* and therefore do not contain ions.

The ammeter should have recorded a current when the salt solutions and the acid and base solutions were connected in the circuit. In solution, salts *dissociate* into their ions, so that these are free to move in the solution. Acids and bases behave in a similar way, and dissociate to form hydronium and oxonium ions. Look at the following examples:

$$\begin{split} \mathrm{KBr} &\rightarrow \mathrm{K}^{+} + \mathrm{Br}^{-} \\ \mathrm{NaCl} &\rightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-} \\ \mathrm{HCl} &+ \mathrm{H_2O} &\rightarrow \mathrm{H_3O^{+} + \mathrm{Cl}^{-}} \\ \mathrm{NaOH} &\rightarrow \mathrm{Na^{+} + \mathrm{OH}^{-}} \end{split}$$

Conclusions:

Solutions that contain free-moving ions are able to conduct electricity because of the movement of charged particles. Solutions that do not contain free-moving ions do not conduct electricity.



Conductivity in streams and rivers is affected by the geology of the area where the water is flowing through. Streams that run through areas with granite bedrock tend to have lower conductivity because granite is made of materials that do not ionise when washed into the water. On the other hand, streams that run through areas with clay soils tend to have higher conductivity because the materials ionise when they are washed into the water. Pollution can also affect conductivity. A failing sewage system or an inflow of fertiliser runoff would raise the conductivity because of the presence of chloride, phosphate, and nitrate (ions) while an oil spill (non-ionic) would lower the conductivity. It is very important that conductivity is kept within a certain acceptable range so that the organisms living in these water systems are able to survive.

20.7 Precipitation reactions

Sometimes, ions in solution may react with each other to form a new substance that is *insoluble*. This is called a **precipitate**.



Definition: Precipitate

A precipitate is the solid that forms in a solution during a chemical reaction.

Activity :: Demonstration : The reaction of ions in solution Apparatus and materials:

4 test tubes; copper(II) chloride solution; sodium carbonate solution; sodium sulphate solution



Method:

- 1. Prepare 2 test tubes with approximately 5 ml of dilute Cu(II)chloride solution in each
- 2. Prepare 1 test tube with 5 ml sodium carbonate solution
- 3. Prepare 1 test tube with 5 ml sodium sulphate solution
- Carefully pour the sodium carbonate solution into one of the test tubes containing copper(II) chloride and observe what happens
- Carefully pour the sodium sulphate solution into the second test tube containing copper(II) chloride and observe what happens

Results:

- 1. A light blue precipitate forms when sodium carbonate reacts with copper(II) chloride
- 2. No precipitate forms when sodium sulphate reacts with copper(II) chloride

It is important to understand what happened in the previous demonstration. We will look at what happens in each reaction, step by step.

1. Reaction 1: Sodium carbonate reacts with copper(II) chloride

When these compounds react, a number of ions are present in solution: Cu^{2+} , Cl^- , Na^+ and CO_3^{2-} .

Because there are lots of ions in solution, they will collide with each other and may recombine in different ways. The product that forms may be insoluble, in which case a precipitate will form, or the product will be soluble, in which case the ions will go back into solution. Let's see how the ions in this example could have combined with each other:

$$\begin{split} \mathrm{Cu}^{2+} + \mathrm{CO}_3^{2-} &\rightarrow \mathrm{Cu}\mathrm{CO}_3\\ \mathrm{Cu}^{2+} + 2\mathrm{Cl}^- &\rightarrow \mathrm{Cu}\mathrm{Cl}_2\\ \mathrm{Na}^+ + \mathrm{Cl}^- &\rightarrow \mathrm{Na}\mathrm{Cl}\\ \mathrm{Na}^+ + \mathrm{CO}_3^{2-} &\rightarrow \mathrm{Na}_2\mathrm{CO}_3 \end{split}$$

You can automatically exclude the reactions where sodium carbonate and copper(II) chloride are the products because these were the initial reactants. You also know that sodium chloride (NaCl) is soluble in water, so the remaining product (copper carbonate) must be the one that is insoluble. It is also possible to look up which salts are soluble and which are insoluble. If you do this, you will find that most carbonates are insoluble, therefore the precipitate that forms in this reaction must be $CuCO_3$. The reaction that has taken place between the ions in solution is as follows:

$$2Na^{+} + CO_{3}^{2-} + Cu^{2+} + 2Cl^{-} \rightarrow CuCO_{3} + 2Na^{+} + 2Cl^{-}$$

2. Reaction 2: Sodium sulphate reacts with copper(II) chloride

The ions that are present in solution are Cu^{2+} , Cl^{-} , Na^{+} and SO_{4}^{2-} .

The ions collide with each other and may recombine in different ways. The possible combinations of the ions are as follows:

$$\begin{split} & \mathrm{Cu}^{2+} + \mathrm{SO}_4^{2-} \rightarrow \mathrm{Cu}\mathrm{SO}_4 \\ & \mathrm{Cu}^{2+} + 2\mathrm{Cl}^- \rightarrow \mathrm{Cu}\mathrm{Cl}_2 \\ & \mathrm{Na}^+ + \mathrm{Cl}^- \rightarrow \mathrm{Na}\mathrm{Cl} \\ & \mathrm{Na}^+ + \mathrm{SO}_4^{2-} \rightarrow \mathrm{Na}_2\mathrm{SO}_4 \end{split}$$

If we look up which of these salts are soluble and which are insoluble, we see that most chlorides and most sulphates are soluble. This is why no precipitate forms in this second reaction. Even when the ions recombine, they immediately separate and go back into solution. The reaction that has taken place between the ions in solution is as follows:

$$2Na^{+} + SO_{4}^{2-} + Cu^{2+} + 2Cl^{-} \rightarrow 2Na^{+} + SO_{4}^{2-} + Cu^{2+} + 2Cl^{-}$$

Table 20.1 shows some of the general rules about the solubility of different salts based on a number of investigations:

Salt	Solubility
Nitrates	All are soluble
Potassium, sodium and ammo-	All are soluble
nium salts	
Chlorides	All are soluble except silver chlo-
	ride, lead(II)chloride and mer-
	cury(II)chloride
Sulphates	All are soluble except
	lead(II)sulphate, barium sul-
	phate and calcium sulphate
Carbonates	All are insoluble except those of
	potassium, sodium and ammo-
	nium

Table 20.1: General rules for the solubility of salts

20.8 Testing for common anions in solution

It is also possible to carry out tests to determine which ions are present in a solution.

20.8.1 Test for a chloride

Prepare a solution of the unknown salt using distilled water and add a small amount of **silver nitrate** solution. If a white precipitate forms, the salt is either a chloride or a carbonate.

$$\rm Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + NO_3^-$$
 (AgCl is white precipitate)
 $\rm CO_3^{2-} + 2Ag^+ + 2NO_3^- \rightarrow Ag_2CO_3 + 2NO_2$ (Ag₂CO₃ is white precipitate)

The next step is to treat the precipitate with a small amount of **concentrated nitric acid**. If the precipitate remains unchanged, then the salt is a chloride. If carbon dioxide is formed, and the precipitate disappears, the salt is a carbonate.

 $AgCl + HNO_3 \rightarrow$ (no reaction; precipitate is unchanged) $Ag_2CO_3 + 2HNO_3 \rightarrow 2AgNO_3 + H_2O + CO_2$ (precipitate disappears)

20.8.2 Test for a sulphate

Add a small amount of barium chloride solution to a solution of the test salt. If a white precipitate forms, the salt is either a sulphate or a carbonate.

$$SO_4^{2-} + Ba^{2+} + Cl^- \rightarrow BaSO_4 + Cl^-$$
 (BaSO₄ is a white precipitate)
 $CO_3^{2-} + Ba^{2+} + Cl^- \rightarrow BaCO_3 + Cl^-$ (BaCO₃ is a white precipitate)

If the precipitate is treated with nitric acid, it is possible to distinguish whether the salt is a sulphate or a carbonate (as in the test for a chloride).

 $BaSO_4 + HNO_3 \rightarrow$ (no reaction; precipitate is unchanged) $BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O + CO_2$ (precipitate disappears)

20.8.3 Test for a carbonate

If a sample of the dry salt is treated with a small amount of acid, the production of carbon dioxide is a positive test for a carbonate.

Acid +
$$CO_3^{2-} \rightarrow CO_2$$

If the gas is passed through limewater and the solution becomes milky, the gas is carbon dioxide.

 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (It is the insoluble CaCO₃ precipitate that makes the limewater go milky)

20.8.4 Test for bromides and iodides

As was the case with the chlorides, the bromides and iodides also form precipitates when they are reacted with silver nitrate. Silver chloride is a white precipitate, but the silver bromide and silver iodide precipitates are both pale yellow. To determine whether the precipitate is a bromide or an iodide, we use chlorine water and carbon tetrachloride (CCl_4).

Chlorine water frees bromine gas from the bromide, and colours the carbon tetrachloride a reddish brown.

Chlorine water frees iodine gas from an iodide, and colours the carbon tetrachloride is coloured purple.



Exercise: Precipitation reactions and ions in solution

- Silver nitrate (AgNO₃) reacts with potassium chloride (KCl) and a white precipitate is formed.
 - (a) Write a balanced equation for the reaction that takes place.
 - (b) What is the name of the insoluble salt that forms?
 - (c) Which of the salts in this reaction are soluble?
- 2. Barium chloride reacts with sulfuric acid to produce barium sulphate and hydrochloric acid.
 - (a) Write a balanced equation for the reaction that takes place.
 - (b) Does a precipitate form during the reaction?
 - (c) Describe a test that could be used to test for the presence of barium sulphate in the products.
- 3. A test tube contains a clear, colourless salt solution. A few drops of silver nitrate solution are added to the solution and a pale yellow precipitate forms. Which one of the following salts was dissolved in the original solution?
 - (a) Nal
 - (b) KCI
 - (c) K_2CO_3
 - (d) Na_2SO_4
 - (IEB Paper 2, 2005)

20.9 Threats to the Hydrosphere

It should be clear by now that the hydrosphere plays an extremely important role in the survival of life on Earth, and that the unique properties of water allow various important chemical processes to take place which would otherwise not be possible. Unfortunately for us however, there are a number of factors that threaten our hydrosphere, and most of these threats are because of human activities. We are going to focus on two of these issues: **overuse** and **pollution** and look at ways in which these problems can possibly be overcome.

1. Overuse of water

We mentioned earlier that only a very small percentage of the hydrosphere's water is available as freshwater. However, despite this, humans continue to use more and more water to the point where water *consumption* is fast approaching the amount of water that is *available*. The situation is a serious one, particularly in countries such as South Africa which are naturally dry, and where water resources are limited. It is estimated that between 2020 and 2040, water supplies in South Africa will no longer be able to meet the growing demand for water in this country. This is partly due to population growth, but also because of the increasing needs of industries as they expand and develop. For each of us, this should be a very scary thought. Try to imagine a day without water...difficult isn't it? Water is so much a part of our lives, that we are hardly aware of the huge part that it plays in our daily lives.

Activity :: Discussion : Creative water conservation

As populations grow, so do the demands that are placed on dwindling water resources. While many people argue that building dams helps to solve this watershortage problem, the reality is that dams are only a temporary solution, and that they often end up doing far more ecological damage than good. The only sustainable solution is to reduce the *demand* for water, so that water supplies are sufficient to meet this. The more important question then is how to do this. **Discussion:**

Divide the class into groups, so that there are about five people in each. Each group is going to represent a different sector within society. Your teacher will tell you which sector you belong to from the following: Farming, industry, city management or civil society (i.e. you will represent the ordinary 'man on the street'). In your groups, discuss the following questions as they relate to the group of people you represent: (Remember to take notes during your discussions, and nominate a spokesperson to give feedback to the rest of the class on behalf of your group)

- What steps could be taken by your group to conserve water?
- Why do you think these steps are *not* being taken?
- What incentives do you think could be introduced to encourage this group to conserve water more efficiently?

2. Pollution

Pollution of the hydrosphere is also a major problem. When we think of pollution, we sometimes only think of things like plastic, bottles, oil and so on. But any chemical that is present in the hydrosphere in an amount that is not what it should be is a pollutant. Animals and plants that live in the hydrosphere are specially adapted to surviving within a certain range of conditions. If these conditions are changed (e.g. through pollution), these organisms may not be able to survive. Pollution then, can affect entire aquatic ecosystems. The most common forms of pollution in the hydrosphere are *waste products* from humans and from industries, *nutrient pollution* e.g. fertiliser runoff which causes eutrophication (this will be discussed in a later section) and toxic trace elements such as aluminium, mercury and copper to name a few. Most of these elements come from mines or from industries.

It is important to realise that our hydrosphere exists in a delicate balance with other systems, and that disturbing this balance can have serious consequences for life on this planet.

Activity :: Group Project : School Action Project

There is a lot that can be done within a school to save water. As a class, discuss what actions could be taken by your class to make people more aware of how important it is to conserve water.

20.10 Summary

- The **hydrosphere** includes all the water that is on Earth. Sources of water include freshwater (e.g. rivers, lakes), saltwater (e.g. oceans), groundwater (e.g. boreholes) and water vapour. Ice (e.g. glaciers) is also part of the hydrosphere.
- The hydrosphere interacts with other global systems, including the atmosphere, lithosphere and biosphere.
- The hydrosphere has a number of important functions. Water is a part of all living cells, it provides a habitat for many living organisms, it helps to regulate climate, and it is used by humans for domestic, industrial and other use.
- The polar nature of water means that ionic compounds dissociate easily in aqueous solution into their component ions.
- **lons** in solution play a number of roles. In the human body for example, ions help to regulate the internal environment (e.g. controlling muscle function, regulating blood pH). lons in solution also determine water hardness and pH.
- Water hardness is a measure of the mineral content of water. Hard water has a high mineral concentration and generally also a high concentration of metal ions e.g. calcium and magnesium. The opposite is true for soft water.
- **pH** is a measure of the concentration of hydrogen ions in solution. The formula used to calculate pH is as follows:

$$pH = -log[H_3O^+]$$
 or $pH = -log[H^+]$

A solution with a pH less than 7 is considered acidic and more than 7 is considered basic (or alkaline). A neutral solution has a pH of 7.

- Gases such as CO₂, NO₂ and SO² dissolve in water to form weak acid solutions. Rain is naturally acidic because of the high concentrations of carbon dioxide in the atmosphere. Human activities such as burning fossil fuels, increase the concentration of these gases in the atmosphere, resulting in **acid rain**.
- Conductivity is a measure of a solution's ability to conduct an electric current.
- An **electrolyte** is a substance that contains free ions, and is therefore able to conduct an electric current. Electrolytes can be divided into **strong** and **weak** electrolytes, based on the extent to which the substance ionises in solution.
- A **non-electrolyte** cannot conduct an electric current because it dooes not contain free ions.
- The **type of substance**, the **concentration of ions** and the **temperature** of the solution, affect its conductivity.

- A **precipitate** is formed when ions in solution react with each other to form an insoluble product. Solubility 'rules' help to identify the precipitate that has been formed.
- A number of tests can be used to identify whether certain anions are present in a solution.
- Despite the importance of the hydrosphere, a number of factors threaten it. These include **overuse** of water, and **pollution**.

Exercise: Summary Exercise

- 1. Give one word for each of the following descriptions:
 - (a) the change in phase of water from a gas to a liquid
 - (b) a charged atom
 - (c) a term used to describe the mineral content of water
 - (d) a gas that forms sulfuric acid when it reacts with water
- 2. Match the information in column A with the information in column B by writing only the letter (A to I) next to the question number (1 to 7)

Column A	Column B
1. A polar molecule	A. H_2SO_4
2. molecular solution	B. CaCO $_3$
3. Mineral that increases water hardness	C. NaOH
4. Substance that increases the hydrogen ion concentration	D. salt water
5. A strong electrolyte	E. calcium
6. A white precipitate	F. carbon dioxide
7. A non-conductor of electricity	G. potassium nitrate
	H. sugar water
	I. O ₂

- 3. For each of the following questions, choose the one correct answer from the list provided.
 - (a) Which one of the following substances does not conduct electricity in the solid phase but is an electrical conductor when molten?

i. Cu

- ii. Pb Br_2
- iii. H_2O
- iv. I_2

(IEB Paper 2, 2003)

- (b) The following substances are dissolved in water. Which one of the solutions is basic?
 - i. sodium nitrate
 - ii. calcium sulphate
 - iii. ammonium chloride
 - iv. potassium carbonate
 - (IEB Paper 2, 2005)
- 4. The concentration of hydronium and hydroxyl ions in a typical sample of seawater are 10^{-8} and 10^{-6} respectively.
 - (a) Is the seawater acidic or basic?
 - (b) Calculate the pH of this seawater.
- 5. Three test tubes (X, Y and Z) each contain a solution of an unknown potassium salt. The following observations were made during a practical investigation to identify the solutions in the test tubes:

A: A white precipitate formed when silver nitrate (AgNO_3) was added to test tube Z.

B: A white precipitate formed in test tubes X and Y when barium chloride (BaCl_2) was added.

C: The precipitate in test tube X dissolved in hydrochloric acid (HCl) and a gas was released.

- D: The precipitate in test tube Y was insoluble in hydrochloric acid.
- (a) Use the above information to identify the solutions in each of the test tubes X, Y and Z.
- (b) Write a chemical equation for the reaction that took place in test tube X before hydrochloric acid was added.

(DoE Exemplar Paper 2 2007)

Chapter 21

The Lithosphere - Grade 11

(NOTE TO SELF: Need map showing major mining areas in SA)

21.1 Introduction

If we were to cut the Earth in half we would see that our planet is made up of a number of layers, namely the **core** at the centre, the **mantle** and the outer **crust** (figure 21.1). The core is made up mostly of iron. The mantle, which lies between the core and the crust, consists of molten rock, called **magma** which moves continuously because of convection currents. The crust is the thin, hard outer layer that 'floats' on the magma of the mantle. It is the upper part of the mantle and the crust that make up the **lithosphere** ('lith' means 'types of stone' and 'sphere' refers to the round shape of the earth). Together, the lithosphere, hydrosphere and atmosphere make up the world as we know it.



Figure 21.1: A cross-section through the earth to show its different layers



Definition: Lithosphere

The lithosphere is the solid outermost shell of our planet. The lithosphere includes the crust and the upper part of the mantle, and is made up of material from both the continents and the oceans on the Earth's surface. Earlier chapters have focused on the hydrosphere (chapter 20) and the atmosphere (chapter 22). The lithosphere is also very important, not only because it is the surface on which we live, but also because humans gain many valuable resources from this part of the planet.

21.2 The chemistry of the earth's crust

The crust is made up of about 80 elements, which occur in over 2000 different compounds and minerals. However, most of the mass of crustal material is made up of only 8 of these elements. These are oxygen (O), silica (Si), aluminium (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K) and magnesium (Mg). These metal elements are seldom found in their pure form, but are usually part of other more complex **minerals**. A mineral is a compound that is formed through geological processes, which give it a particular structure. A mineral could be a pure element, but more often minerals are made up of many different elements combined. *Quartz* is just one example. It is a mineral that is made up of silica and oxygen. Some more examples are shown in table 21.1.



Definition: Mineral

Minerals are natural compounds formed through geological processes. The term 'mineral' includes both the material's chemical composition and its structure. Minerals range in composition from pure elements to complex compounds.

Mineral	Chemistry	Comments
Quartz	SiO_2 (silicon dioxide)	Quartz is used for glass, in electrical com-
		ponents, optical lenses and in building
		stone
Gold	Au (pure element) or	Gold is often found in a group of miner-
	AuTe $_2$ (Calaverite, a gold	als called the <i>tellurides</i> . Calaverite is a
	mineral)	mineral that belongs to this group, and is
		the most common gold-bearing mineral.
		Gold has an affinity for tellurium (Te).
Hematite	Fe_2O_3 (iron oxide)	Iron usually occurs in iron oxide minerals
		or as an alloy of iron and nickel.
Orthoclase	KAlSi $_3$ O $_8$ (potassium alu-	Orthoclase belongs to the <i>feldspar</i> group
	minium silicate)	of minerals.
Copper	Cu (pure element) or	copper can be mined as a pure element
	$Cu_2(CO_3)(OH)_2$ (mala-	or as a mineral such as malachite.
	chite or copper carbonate	
	hydroxide)	

Table 21.1: Table showing examples of minerals and their chemistry

A **rock** is a combination of one or more minerals. *Granite* for example, is a rock that is made up of minerals such as SiO_2 , Al_2O_3 , CaO, K_2O , Na_2O and others. There are three different types of rocks, **igneous**, **sedimentary** and **metamorphic**. Igneous rocks (e.g. granite, basalt) are formed when magma is brought to the earth's surface as lava, and then solidifies. Sedimentary rocks (e.g. sandstone, limestone) form when rock fragments, organic matter or other sediment particles are deposited and then compacted over time until they solidify. Metamorphic rock is formed when any other rock types are subjected to intense heat and pressure over a period of time. Examples include slate and marble.

Many of the elements that are of interest to us (e.g. gold, iron, copper), are unevenly distributed in the lithosphere. In places where these elements are abundant, it is profitable to extract them (e.g. through mining) for economic purposes. If their concentration is very low, then the cost of extraction becomes more than the money that would be made if they were sold. Rocks that contain valuable minerals are called **ores**. As humans, we are particularly interested in the ores that contain metal elements, and also in those minerals that can be used to produce energy.



Definition: Ore

An ore is a volume of rock that contains minerals which make it valuable for mining.



A gemstone (also sometimes called a gem or semi-precious stone), is a highly attractive and valuable piece of mineral which, when cut and polished, is used in jewelry and other adornments. Examples of gemstones are amethyst, diamond, cat's eye and sapphire.



Exercise: Rocks and minerals

- 1. Where are most of the earth's minerals concentrated?
- 2. Explain the difference between a mineral, a rock and an ore.
- 3. Carry out your own research to find out which elements are found in the following minerals:
 - (a) gypsum
 - (b) calcite
 - (c) topaz

4. Which minerals are found in the following rocks?

- (a) basalt
- (b) sandstone
- (c) marble

21.3 A brief history of mineral use

Many of the minerals that are important to humans are **metals** such as gold, aluminium, copper and iron. Throughout history, metals have played a very important role in making jewelery, tools, weapons and later machinery and other forms of technology. We have become so used to having metals around us that we seldom stop to think what life might have been like before metals were discovered. During the **Stone Age** for example, **stones** were used to make tools. Slivers of stone were cut from a rock and then sharpened. In Africa, some of the stone tools that have been found date back to 2.5 million years ago!

It was the discovery of *metals* that led to some huge advances in agriculture, warfare, transport and even cookery. One of the first metals to be discovered was **gold**, probably because of its beautiful shiny appearance. Gold was used mostly to make jewelery because it was too soft to make harder tools. Later, **copper** became an important metal because it could be hammered into shape, and it also lasted a lot longer than the stone that had previously been used in knives, cooking utensils and weapons. Copper can also be melted and then put into a mould to re-shape it. This is known as **casting**.

At about the time that copper was in widespread use, it was discovered that if certain kinds of stones are heated to high enough temperatures, liquid metals flow from them. These rocks are

ores, and contain the metal minerals inside them. The process of heating mineral ores in this way is called **smelting**. It was also found that ores do not only occur at the earth's surface, but also deep *below* it. This discovery led to the beginning of **mining**.

But humans' explorations into the world of metals did not end here! In some areas, the ores of *iron* and *tin* were found close together. The cast alloy of these two metals is **bronze**. Bronze is a very useful metal because it produces a sharper edge than copper. Another important discovery was that of **iron**. Iron is the most abundant metal at the earth's surface but it is more difficult to work with than copper or tin. It is very difficult to extract iron from its ore because it has an extremely high melting point, and only specially designed furnaces are able to produce the temperatures that are needed. An important discovery was that if iron is heated in a furnace with *charcoal*, some of the carbon in the charcoal is transferred to the iron, making the metal even harder. If this hot metal has its temperature reduced very suddenly, it becomes even harder and produces **steel**. Today, steel is a very important part of industry and construction.



Originally it was believed that much of Africa's knowledge of metals and their uses was from the Middle East. But this may not be the case. More recent studies have shown that iron was used far earlier than it would have been if knowledge of this metal had started in the Middle East. Many metal technologies may in fact have developed independently in Africa and in many African countries, metals have an extremely important place in society. In Nigeria's Yoruba country for example, iron has divine status because it is used to make instruments for survival. 'Ogun', the God of Iron, is seen as the protector of the kingdom.

21.4 Energy resources and their uses

Apart from minerals and ores, the products of the lithosphere are also important in meeting our energy needs.

Coal is one of the most important fuels that is used in the production of electricity. Coal is formed from organic material when plants and animals decompose, leaving behind organic remains that accumulate and become compacted over millions of years under sedimentary rock. The layers of compact organic material that can be found between sedimentary layers, are coal. When coal is burned, a large amount of heat energy is released, which is used to produce electricity. South Africa is the world's sixth largest coal producer, with Mpumalanga contributing about 83

Another element that is found in the crust, and which helps to meet our energy needs, is **uranium**. Uranium produces energy through the process of *nuclear fission*. Neutrons are aimed at the nucleii of the uranium atoms in order to split them. When the nucleus of a uranium atom is split, a large amount of energy is released as heat. This heat is used to produce steam, which turns turbines to generate electricity. Uranium is produced as a by-product of gold in some mines in the Witwatersrand, and as a by-product in some copper mines, for example in Phalaborwa. This type of nuclear power is relatively environmentally friendly since it produces low gas emissions. However, the process does produce small amounts of radioactive wastes , which must be carefully disposed of in order to prevent contamination.

Oil is another product of the lithosphere which is critical in meeting our fuel needs. While most of South Africa's oil is imported and then processed at a refinery in either Durban, Cape Town or Sasolburg, some is extracted from coal. The technology behind this type of extraction has largely been developed by SASOL (South African Coal, Oil and Gas Corporation). Oil, like coal,

is organic in origin and normally forms from organic deposits on the ocean floor. Oil requires unique geological and geochemical conditions in order to be produced. Part of this process involves the burial of organic-rich sediments under extremely high temperatures and pressures. The oil that is produced is then pushed out into nearby sedimentary layers. Oil will then move upwards until it is trapped by an impermeable rock layer. It accumulates here, and can then be accessed by oil rigs and other advanced equipment.

21.5 Mining and Mineral Processing: Gold

21.5.1 Introduction

Gold was discovered in South Africa in the late 1800's and since then has played a very important role in South Africa's *history* and *economy*. Its discovery brought many foreigners into South Africa, who were lured by the promises of wealth. They set up small mining villages, which later grew into larger settlements, towns and cities. One of the first of these settlements was the beginning of present-day Johannesburg, also known as 'Egoli' or 'Place of Gold'.

Most of South Africa's gold is concentrated in the 'Golden Arc', which stretches from Johannesburg to Welkom. Geologists believe that, millions of years ago, this area was a massive inland lake. Rivers feeding into this lake brought sand, silt, pebbles and fine particles of gold and deposited them over a long period of time. Eventually these deposits accumulated and became compacted to form gold-bearing sedimentary rock or **gold reefs**. It is because of this complex, but unique, set of circumstances that South Africa's gold deposits are so concentrated in that area. In other countries like Zimbabwe, gold occurs in smaller 'pockets', which are scattered over a much greater area.

21.5.2 Mining the Gold

A number of different techniques can be used to mine gold. The three most common methods in South Africa are **panning**, **open cast** and **shaft** mining.

1. Panning

Panning for gold is a manual technique that is used to sort gold from other sediments. Wide, shallow pans are filled with sand and gravel (often from river beds) that may contain gold. Water is added and the pans are shaken so that the gold is sorted from the rock and other materials. Because gold is much more dense, it settles to the bottom of the pan. **Pilgrim's Rest** in Mpumalanga, was the first site for gold panning in South Africa.

2. Open cast mining

This is a form of surface mining. Surface layers of rock and sediments are removed so that the deeper gold rich layers can be reached. This type of mining is not suitable if the gold is buried very deep below the surface.

3. Shaft mining

South Africa's thin but extensive gold reefs slope at an angle underneath the ground, and this means that some deposits are very deep and often difficult to reach. Shaft mining is needed to reach the gold ore. After the initial drilling, blasting and equipping of a mine shaft, tunnels are built leading outwards from the main shaft so that the gold reef can be reached. Shaft mining is a dangerous operation, and roof supports are needed so that the rock does not collapse. There are also problems of the intense heat and high pressure below the surface which make shaft mining very complex, dangerous and expensive. A diagram illustrating open cast and shaft mining is shown in figure 21.2.

21.5.3 Processing the gold ore

For every ton of ore that is mined, only a very small amount of gold is extracted. A number of different methods can be used to separate gold from its ore, but one of the more common



Figure 21.2: Diagram showing open cast and shaft mining

methods is called gold cyanidation.

In the process of gold cyanidation, the ore is crushed and then cyanide solution is added so that the gold particles are chemically dissolved from the ore. In this step of the process, gold is oxidised. Zinc dust is then added to the cyanide solution. The zinc takes the place of the gold, so that the gold is precipitated out of the solution. This process is shown in figure 21.3.



Another method that is used to process gold is called the 'carbon-in-pulp' (CIP) method. This method makes use of the high affinity that activated carbon has for gold, and there are three stages to the process. The first stage involves the *absorption* of gold in the cyanide solution to carbon. In the *elution* stage, gold is removed from the carbon into an alkaline cyanide solution. In the final stage, *electro-winning* is used to remove gold from the solution through a process of electrolysis. Gold that has been removed is deposited on steel wool electrodes. Both the carbon and the acid are then treated so that they can be re-used.

21.5.4 Characteristics and uses of gold

Gold has a number of uses because of its varied and unique characteristics. Below is a list of some of these characteristics that have made gold such a valuable metal:

• Shiny

Gold's beautiful appearance has made it one of the favourite metals for use in jewelery.



Figure 21.3: Flow diagram showing how gold is processed

• Durable

Gold does not tarnish or corrode easily, and therefore does not deteriorate in quality. It is sometimes used in dentistry to make the crowns for teeth.

• Malleable and ductile

Since gold can be bent and twisted into shape, as well as being flattened into very thin sheets, it is very useful in fine wires and to produce sheets of gold.

• Good conductor

Gold is a good conductor of electricity and is therefore used in transistors, computer circuits and telephone exchanges.

• Heat ray reflector

Because gold reflects heat very effectively, it is used in space suits and in vehicles. It is also used in the protective outer coating of artificial satellites. One of the more unusual applications of gold is its use in firefighting, where a thin layer of gold is placed in the masks of the firefighters to protect them from the heat.

Activity :: Case Study : Dropping like a gold balloon

Read the article below, which has been adapted from one that appeared in the *Financial Mail* on 15th April 2005 and then answer the questions that follow.

As recently as 1980, South Africa accounted for over 70% of world gold production. In 2004, that figure was a dismal 14%. Chamber of Mines figures showed that SA's annual gold production last year slipped to its lowest level since 1931.

Chamber economist Roger Baxter says the 'precipitous' fall in production was caused by the dual impact of the fall in the rand gold price due to the strong rand, and the continued upward rise in costs. Many of these costs, laments Baxter, are 'costs we do not have control over'. These include

water, transport, steel and labour costs, which rose by 13% on average in 2004.

He provides a breakdown of the cost components faced by mines:

- Water prices have risen by 10% per year for the past 3 years
- Steel prices have increased by double-digit rates for each of the past 3 years
- Spoornet's tariffs rose 35% in 2003 and 16.5% in 2004
- Labour costs, which make up 50% of production costs, rose above inflation in 2003 and 2004

At these costs, and at current rand gold prices, about 10 mines, employing 90 000 people, are marginal or loss-making, says Baxter.

1. Refer to the table below showing SA's gold production in tons between 1980 and 2004.

Year	Production
	(t)
1980	675
1985	660
1990	600
1995	525
2000	425
2004	340

Draw a line graph to illustrate these statistics.

- What percentage did South Africa's gold production contribute towards global production in:
 - (a) 1980
 - (b) 2004
- 3. Outline two reasons for this drop in gold production.
- 4. Briefly explain how the increased cost of resources such as water contributes towards declining profitability in gold mines.
- 5. Suggest a reason why the cost of *steel* might affect gold production.
- 6. Suggest what impact a decrease in gold production is likely to have on...
 - (a) South Africa's economy
 - (b) mine employees
- 7. Find out what the current price of gold is. Discuss why you think gold is so expensive.

21.5.5 Environmental impacts of gold mining

However, despite the incredible value of gold and its usefulness in a variety of applications, all mining has an environmental cost. The following are just a few of the environmental impacts of gold mining:

• Resource consumption

Gold mining needs large amounts of electricity and water.

Poisoned water

Acid from gold processing can leach into nearby water systems such as rivers, causing damage to animals and plants, as well as humans that may rely on that water for drinking. The disposal of other toxic waste (e.g. cyanide) can also have a devastating effect on biodiversity.

Solid waste

This applies particularly to open pit mines, where large amounts of soil and rock must be displaced in order to access the gold reserves. Processing the gold ore also leaves solid waste behind.

• Air pollution

Dust from open pit mines, as well as harmful gases such as sulfur dioxide and nitrogen dioxide which are released from the furnaces, contribute to air pollution.

• Threaten natural areas

Mining activities often encroach on protected areas and threaten biodiversity in their operation areas.

Activity :: Discussion : Mine rehabilitation

There is a growing emphasis on the need to rehabilitate old mine sites that are no longer in use. If it is too difficult to restore the site to what it was before, then a new type of land use might be decided for that area. Any mine rehabilitation programme should aim to achieve the following:

- ensure that the site is safe and stable
- remove pollutants that are contaminating the site
- restore the biodiversity that was there before mining started
- restore waterways to what they were before mining

There are different ways to achieve these goals. Plants for example, can be used to remove metals from polluted soils and water, and can also help to stabilise the soil so that other vegetation can grow. Land contouring can help to restore drainage in the area.

Discussion:

In groups of 3-4, discuss the following questions:

- 1. What are the main benefits of mine rehabilitation?
- 2. What are some of the difficulties that may be experienced in trying to rehabilitate a mine site?
- 3. Suggest some creative ideas that could be used to encourage mining companies to rehabilitate old sites.
- 4. One rehabilitation project that has received a lot of publicity is the rehabilitation of dunes that were mined for titanium by Richards Bay Minerals (RBM). As a group, carry out your own research to try to find out more about this project.
 - What actions did RBM take to rehabilitate the dunes?
 - Was the project successful?
 - What were some of the challenges faced?



Exercise: Gold mining

Mapungubwe in the Limpopo Province is evidence of gold mining in South Africa as early as 1200. Today, South Africa is a world leader in the technology of gold mining. The following flow diagram illustrates some of the most important steps in the recovery of gold from its ore.



- 1. Name the process indicated by A.
- 2. During process A, gold is extracted from the ore. Is gold oxidised or reduced during this process?
- 3. Use oxidation numbers to explain your answer to the question above.
- 4. Name the chemical substance that is used in process B.
- 5. During smelting (illustrated by C in the diagram), gold is sent into a calcining furnace. Briefly explain the importance of this process taking place in the furnace.
- 6. The recovery of gold can have a negative impact on water in our country, if not managed properly. State at least one negative influence that the recovery of gold can have on water resources and how it will impact on humans and the environment.

21.6 Mining and mineral processing: Iron

Iron is one of the most abundant metals on Earth. Its concentration is highest in the core, and lower in the crust. It is extracted from **iron ore** and is almost never found in its elemental form. Iron ores are usually rich in **iron oxide** minerals and may vary in colour from dark grey to rusty red. Iron is usually found in minerals such as magnetite (Fe_3O_4) and hematite (Fe_2O_3). Iron ore also contains other elements, which have to be removed in various ways. These include silica (Si), phosphorus (P), aluminium (AI) and sulfur (S).

21.6.1 Iron mining and iron ore processing

One of the more common methods of mining for iron ore is **open cast mining**. Open cast mining is used when the iron ore is found near the surface. Once the ore has been removed, it needs to be crushed into fine particles before it can be processed further.

As mentioned earlier, iron is commonly found in the form of **iron oxides**. To create pure iron, the ore must be **smelted** to remove the oxygen.



Definition: Smelting

Smelting is a method used to extract a metal from its ore and then purify it.

Smelting usually involves heating the ore and also adding a reducing agent (e.g. carbon) so that the metal can be freed from its ore. The bonds between iron and oxygen are very strong, and therefore it is important to use an element that will form stronger bonds with oxygen that the iron. This is why carbon is used. In fact, carbon monoxide is the main ingredient that is needed to strip oxygen from iron. These reactions take place in a **blast furnace**.

A blast furnace is a huge steel container many metres high and lined with heat-resistant material. In the furnace the solid raw materials, i.e. iron ore, carbon (in the form of 'coke', a type of coal) and a flux (e.g. limestone) are fed into the top of the furnace and a blast of heated air is forced into the furnace from the bottom. Temperatures in a blast furnace can reach 2000°C. A simple

diagram of a blast furnace is shown in figure 21.4. The equations for the reactions that take place are shown in the flow diagram below.

STEP 1: Production of carbon monoxide $C+O_2 \rightarrow CO_2$ $CO_2+C \rightarrow 2CO$

STEP 2: Reduction of iron oxides takes place in a number of stages to produce iron. $3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$

> $Fe_3O_4 + CO \rightarrow 3FeO + CO_2$ $FeO + CO \rightarrow Fe + CO_2$

> > STEP 3: Fluxing

The flux is used to melt impurities in the ore. A common flux is limestone (CaCO₃). Common impurities are silica, phosphorus (makes steel brittle), aluminium and sulfur (produces SO_2

gases during smelting and interferes with the smellting process).

 $CaCO_3 \rightarrow CaO + CO_2$

$$CaO + SiO_2 \rightarrow CaSiO_3$$

In step 3, the calcium carbonate breaks down into calcium oxide and carbon dioxide. The calcium oxide then reacts with silicon dioxide (the impurity) to form a **slag**. In this case the slag is the $CaSiO_3$. The slag melts in the furnace, whereas the silicon dioxide would not have, and floats on the more dense iron. This can then be separated and removed.



Figure 21.4: A blast furnace, showing the reactions that take place to produce iron

21.6.2 Types of iron

Iron is the most used of all the metals. Its combination of low cost and high strength make it very important in applications such as industry, automobiles, the hulls of large ships and in the

structural components of buildings. Some of the different forms that iron can take include:

- **Pig iron** is raw iron and is the direct product when iron ore and coke are smelted. It has between 4% and 5% carbon and contains varying amounts of contaminants such as sulfur, silicon and phosphorus. Pig iron is an intermediate step between iron ore, cast iron and steel.
- Wrought iron is commercially pure iron and contains less than 0.2% carbon. It is tough, malleable and ductile. Wrought iron does not rust quickly when it is used outdoors. It has mostly been replaced by mild steel for 'wrought iron' gates and blacksmithing. Mild steel does not have the same corrosion resistance as true wrought iron, but is cheaper and more widely available.
- **Steel** is an alloy made mostly of iron, but also containing a small amount of carbon. Elements other than carbon can also be used to make alloy steels. These include manganese and tungsten. By varying the amounts of the alloy elements in the steel, the following characteristics can be altered: hardness, elasticity, ductility and tensile strength.
- **Corrugated iron** is actually sheets of galvanised steel that have been rolled to give them a corrugated pattern. Corrugated iron is a common building material.

One problem with iron and steel is that pure iron and most of its alloys rust. These products therefore need to be protected from water and oxygen, and this is done through painting, galvanisation and plastic coating.



Iron is also a very important element in all living organisms. One important role that iron plays is that it is a component of the protein **haemoglobin** which is the protein in blood. It is the iron in the haemoglobin that helps to attract and hold oxygen so that this important gas can be transported around the body in the blood, to where it is needed.

21.6.3 Iron in South Africa

The primary steel industry is an important part of the South African economy and it generates a great deal of foreign exchange.

- About 40 million tons of iron ore is mined annually in South Africa. Approximately 15 million tons are consumed locally, and the remaining 25 million tons are exported.
- South Africa is ranked about 20th in the world in terms of its crude steel production.
- South Africa is the largest steel producer in Africa.
- South Africa exports crude steel and finished steel products, and a lot is also used locally.
- Some of the products that are manufactured in South Africa include reinforcing bars, railway track material, wire rod, plates and steel coils and sheets.



Exercise: Iron

Iron is usually extracted from heamatite (iron(III)oxide). Iron ore is mixed with limestone and coke in a blast furnace to produce the metal. The following incomplete word equations describe the extraction process:

- A coke + oxygen \rightarrow gasX
- $\mathsf{B} \;\; \mathsf{gasX} + \mathsf{coke} \to \mathsf{gasY}$
- $\mathsf{C} \ \mathsf{iron}(\mathsf{III})\mathsf{oxide} + \mathsf{gas}\mathsf{Y} \to \mathsf{iron} + \mathsf{gas}\mathsf{X}$
- 1. Name the gases X and Y.
- 2. Write a balanced chemical equation for reaction C.
- 3. What is the function of gas Y in reaction C?
- 4. Why is limestone added to the reaction mixture?
- 5. Briefly describe the impact that the mining of iron has on the economy and the environment in our country.
- (DoE Exemplar Paper, Grade 11, 2007)

21.7 Mining and mineral processing: Phosphates

A phosphate is a salt of **phosphoric acid** (H_3PO_4). Phosphates are the naturally occurring form of the element phosphorus. Phosphorus is seldom found in its pure elemental form, and **phosphate** therefore refers to a rock or ore that contains phosphate ions. The chemical formula for the phosphate ion is PO_4^{3-} .

21.7.1 Mining phosphates

Phosphate is found in beds in sedimentary rock, and has to be quarried to access the ore. A quarry is a type of open pit mine that is used to extract ore. In South Africa, the main phosphate producer is at the Palaborwa alkaline igneous complex, which produces about 3 million tons of ore per year. The ore is crushed into a powder and is then treated with sulfuric acid to form a superphosphate $(Ca(H_2PO_4)_2)$, which is then used as a fertilizer. In the equation below, the phosphate mineral is calcium phosphate $(Ca_3(PO_4)_2)$.

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$$

Alternatively, the ore can be treated with concentrated phosphoric acid, in which case the reaction looks like this:

$$3Ca_3(PO_4)_2.CaF_2 + 4H_3PO_4 + 9H_2O \rightarrow 9Ca(H_2PO_4)_2 + CaF_2$$

21.7.2 Uses of phosphates

Phosphates are mostly used in **agriculture**. Phosphates are one of the three main nutrients needed by plants, and they are therefore an important component of **fertilisers** to stimulate plant growth.



Exploring the lithosphere for minerals is not a random process! **Geologists** help to piece together a picture of what past environments might have been like, so that predictions can be made about where minerals might have a high concentration. **Geophysicists** measure gravity, magnetics and the electrical properties of rocks to try to make similar predictions, while **geochemists** sample the soils at the earth's surface to get an idea of what lies beneath them. You can see now what an important role scientists play in mineral exploration!

?

Exercise: Phosphates

Rock phosphate $[Ca_{10}(PO_4)_6F_2]$, mined from open pit mines at Phalaborwa, is an important raw material in the production of fertilisers. The following two reactions are used to transform rock phosphate into water soluble phosphates:

- A: $Ca_{10}(PO_4)_6F_2 + 7X + 3H_2O \rightarrow 3Ca(H_2PO_4)_2H_2O + 2HF + 7CaSO_4$
- $\mathsf{B:}\ \mathsf{Ca}_{10}(\mathsf{PO}_4)_6\mathsf{F}_2 + \mathsf{14Y} + \mathsf{10H}_2\mathsf{O} \to \mathsf{10Ca}(\mathsf{H}_2\mathsf{PO}_4)_2\mathsf{H}_2\mathsf{O} + \mathsf{2HF}_2\mathsf{O}$
- 1. Identify the acids represented by X and Y.
- 2. Despite similar molecular formulae, the products $Ca(H_2PO_4)_2$ formed in the two reactions have different common names. Write down the names for each of these products in reactions A and B.
- 3. Refer to the products in reactions A and B and write down TWO advantages of reaction B over reaction A.
- 4. Why is rock phosphate unsuitable as fertiliser?
- 5. State ONE advantage and ONE disadvantage of phosphate mining.

(DoE Exemplar Paper, Grade 11, 2007)

Activity :: Case Study : Controversy on the Wild Coast - Titanium mining Read the extract below, which has been adapted from an article that appeared in the Mail and Guardian on 4th May 2007, and then answer the questions that follow.

A potentially violent backlash looms in Pondoland over efforts by an Australian company to persuade villagers to back controversial plans to mine an environmentally sensitive strip of the Wild Coast. The mining will take place in the Xolobeni dunes, south of Port Edward. The application has outraged environmental groups, largely because the proposed mining areas form part of the Pondoland centre of endemism, which has more species than the United Kingdom, some of which are endemic and facing extinction.

Exploratory drilling revealed Xolobeni has the world's 10th largest titanium deposit, worth about R11 billion. The amount of money that will be spent over the mine's 22 years, including a smelter, is estimated at R1.4 billion. The Australian mining company predicts that 570 direct jobs will be created.

But at least two communities fiercely oppose the mining plans. Some opponents are former miners who fear Gauteng's mine dumps and compounds will be replicated on the Wild Coast. Others are employees of failed ecotourism ventures, who blame the mining company for their situation. Many are suspicious of outsiders. The villagers have also complained that some of the structures within the mining company are controlled by business leaders with political connections, who are in it for their own gain. Intimidation of people who oppose the mining has also been alleged. Headman Mandoda Ndovela was shot dead after his outspoken criticism of the mining.

Mzamo Dlamini, a youth living in one of the villages that will be affected by the mining, said 10% of the Amadiba 'who were promised riches by the mining company' support mining. 'The rest say if people bring those machines, we will fight.'

- 1. Explain what the following words means:
 - (a) endemic
 - (b) smelter
 - (c) ecotourism
- 2. What kinds of 'riches' do you think the Amadiba people have been promised by the mining company?
- 3. In two columns, list the potential **advantages** and **disadvantages** of mining in this area.
- 4. Imagine that you were one of the villagers in this area. Write down *three questions* that you would want the mining company to answer before you made a decision about whether to oppose the mining or not. Share your ideas with the rest of the class.
- 5. Imagine that you are an environmentalist. What would your main concerns be about the proposed mining project? Again share your answers with the rest of the class.

21.8 Energy resources and their uses: Coal

The products of the lithosphere are also important in meeting our **energy needs**. Coal is one product that is used to produce energy. In South Africa, coal is particularly important because most of our electricity is generated using coal as a fuel. South Africa is the world's sixth largest coal producer, with Mpumalanga contributing about 83% of our total production. Other areas in which coal is produced, include the Free State, Limpopo and KwaZulu-Natal. One of the problems with coal however, is that it is a **non-renewable resource**, meaning that once all resources have been used up, it cannot simply be produced again. Burning coal also produces large quantities of greenhouse gases, which may play a role in global warming. At present, ESKOM, the South African government's electric power producer, is the coal industry's main customer.

21.8.1 The formation of coal

Coal is what is known as a **fossil fuel**. A fossil fuel is a *hydrocarbon* that has been formed from organic material such as the remains of plants and animals. When plants and animals decompose, they leave behind organic remains that accumulate and become compacted over millions of years under sedimentary rock. Over time, the *heat* and *pressure* in these parts of the earth's crust also increases, and coal is formed. When coal is burned, a large amount of heat energy is released, which is used to produce electricity. **Oil** is also a fossil fuel and is formed in a similar way.



Definition: Fossil Fuel

A fossil fuel is a hydrocarbon that is formed from the fossilised remains of dead plants and animals that have been under conditions of intense heat and pressure for millions of years.

21.8.2 How coal is removed from the ground

Coal can be removed from the crust in a number of different ways. The most common methods used are *strip mining*, *open cast mining* and *underground mining*.

1. Strip mining

Strip mining is a form of surface mining that is used when the coal reserves are very shallow. The *overburden* (overlying sediment) is removed so that the coal seams can be reached. These sediments are replaced once the mining is finished, and in many cases, attempts are made to *rehabilitate* the area.

2. Open cast mining

Open cast mining is also a form of surface mining, but here the coal deposits are too deep to be reached using strip mining. One of the environmental impacts of open cast mining is that the overburden is dumped somewhere else away from the mine, and this leaves a huge pit in the ground.

3. Underground mining

Undergound mining is normally used when the coal seams are amuch deeper, usually at a depth greater than 40 m. As with shaft mining for gold, the problem with underground mining is that it is very dangerous, and there is a very real chance that the ground could collapse during the mining if it is not supported. One way to limit the danger is to use *pillar support* methods, where some of the ground is left unmined so that it forms pillars to support the roof. All the other surfaces underground will be mined. Using another method called *longwalling*, the roof is allowed to collapse as the mined-out area moves along. In South Africa, only a small percentage of coal is mined in this way.

21.8.3 The uses of coal

Although in South Africa, the main use of coal is to produce electricity, it can also be used for other purposes.

1. Electricity

In order to generate electricity, solid coal must be crushed and then burned in a furnace with a boiler. A lot of steam is produced and this is used to spin turbines which then generate electricity.

2. Gasification

If coal is broken down and subjected to very high temperatures and pressures, it forms a *synthesis gas*, which is a mix of carbon dioxide and hydrogen gases. This is very important in the *chemical industry* (refer to chapter 23).

3. Liquid fuels

Coal can also be changed into liquid fuels like petrol and diesel using the **Fischer-Tropsch process**. In fact, South Africa is one of the leaders in this technology (refer to chapter 23). The only problem is that producing liquid fuels from coal, rather than refining petroleum that has been drilled, releases much greater amounts of carbon dioxide into the atmosphere, and this contributes further towards global warming.

21.8.4 Coal and the South African economy

In South Africa, the coal industry is second only to the gold industry. More than this, South Africa is one of the world's top coal *exporters*, and also one of the top *producers*. Of the coal that is produced, most is used locally to produce electricity and the rest is used in industry and domestically.

The problem with coal however, is that it is a **non-renewable resource** which means that once all the coal deposits have been mined, there will be none left. Coal takes such a long time to form, and requires such specific environmental conditions, that it would be impossible for coal to re-form at a rate that would keep up with humankind's current consumption. It is therefore very important that South Africa, and other countries that rely on coal, start to look for alternative energy resources.

21.8.5 The environmental impacts of coal mining

There are a number of environmental impacts associated with coal mining.

• Visual impact and landscape scars

Coal mining leaves some very visible scars on the landscape, and destroys biodiversity (e.g. plants, animals). During strip mining and open cast mining, the visual impact is particularly bad, although this is partly reduced by rehabilitation in some cases.

• Spontaneous combustion and atmospheric pollution

Coal that is left in mine dumps may spontaneously combust, producing large amounts of sulfurous smoke which contributes towards atmospheric pollution.

Acid formation

Waste products from coal mining have a high concentration of sulfur compounds. When these compounds are exposed to water and oxygen, sulfuric acid is formed. If this acid washes into nearby water systems, it can cause a lot of damage to the ecosystem. Acid can also leach into soils and alter its acidity. This in turn affects what will be able to grow there.

Global warming

As was discussed earlier, burning coal to generate electricity produces *carbon dioxide* and *nitrogen oxides* which contribute towards global warming (refer to chapter 22). Another gas that causes problems is *methane*. All coal contains methane, and deeper coal contains the most methane. As a greenhouse gas, methane is about twenty times more potent than carbon dioxide.

Int Fac

It is easy to see how mining, and many other activities including industry and vehicle transport, contribute towards Global Warming. It was for this reason that South Africa joined the **Carbon Sequestration Leadership Forum (CSLF)**. The forum is an international climate change initiative that focuses on developing cost effective technologies to separate and capture carbon dioxide from the atmosphere so that it can be stored in some way. The CSLF also aims to make these technologies as widely available as possible.



- 1. "Coal is as old as the hills, and just as natural." Is this statement TRUE? Motivate your answer by referring to how coal is formed.
- Coal is a non-renewable energy source. Quote a statement from the advertisement that gives an indication that coal is non-renewable. Give a reason for your choice.
- 3. Is coal actually a healthy source of energy? Motivate your answer by referring to all influences that coal and coal mining have on both humans and the environment.
- 4. Why is coal used as a primary energy source in South Africa?

(DoE Exemplar Paper 2, Grade 11, 2007)

21.9 Energy resources and their uses: Oil

Oil is another product of the lithosphere which is very important in meeting our fuel needs.

21.9.1 How oil is formed

Oil is formed in a very similar way to coal, except that the organic material is laid down in **oceans**. Organisms such as zooplankton and algae settle to the ocean floor and become buried under layers of mud. Over time, as these layers of sediment accumulate and the heat and pressure also increase, the organic material changes to a waxy material called *kerogen*. Eventually, with continuing heat and pressure, liquid and gas **hydrocarbons** are formed. These hydrocarbons are lighter than rock and therefore move upwards through the rock layers before being trapped by an impermeable layer. Here the oil will slowly accumulate until there is enough that it can be accessed by oil rigs and other equipment. **Crude oil** or **petroleum**, is actually a mixture of hydrocarbons (mostly alkanes) of different lengths, ranging from 5 carbons to 18 carbons in the hydrocarbon chain. If the mixture contains mostly short hydrocarbons, then it is a gas called **natural gas**. As the hydrocarbon chains in the mixture become longer, the product becomes more and more solid. Coal is made up of the longest hydrocarbons. For more information on hydrocarbons, refer to chapter 9.

21.9.2 Extracting oil

When enough oil has accumulated in a well, it becomes economically viable to try to extract it either through **drilling** or **pumping**. If the pressure in the oil reservoir is high, the oil is forced

naturally to the surface. This is known as *primary recovery* of oil. If the pressure is low, then pumps must be used to extract it. This is known as *secondary recovery*. When the oil is very difficult to extract, steam injection into the reservoir can be used to heat the oil, reduce its viscosity and make it easier to extract.

While most of South Africa's oil is imported and then processed at a refinery in either Durban, Cape Town or Sasolburg, some is extracted from coal, as discussed in section 21.8.

21.9.3 Other oil products

Oil can also be used to make a variety of different products. You will find more information on this in chapter 23.

• Fractional distillation

Fractional distillation is the separation of a mixture into the parts that make it up. In oil refineries, crude oil is separated into useful products such as asphalt, diesel, fuel oil, gasoline, kerosine, liquid petroleum gas (LPG) and tar, to name just a few.

• Cracking

There are two types of cracking, *steam cracking* and *hydrocracking*. Cracking is used to change heavy hydrocarbons such as petroleum into lighter hydrocarbons such as fuels (LPG and gasoline), plastics (ethylene) and other products that are needed to make fuel gas (propylene).

21.9.4 The environmental impacts of oil extraction and use

Some of the key environmental impacts associated with the extraction and use of oil are as follows:

• Pollution

Exploring the oceans for oil, and the actual drilling process, can result in major pollution.

• Ecosystem impacts

Dredging the ocean floors for oil can disrupt seabed ecosystems.

• Global warming

Burning oil as a fuel source produces carbon dioxide, which contributes towards global warming.

21.10 Alternative energy resources

As the world's population increases, so does the demand for energy. As we have already mentioned, many of our energy resources are **non-renewable** and will soon run out. In addition, many of the fuels that we use produce large amounts of greenhouse gases, which can contribute towards global warming. If we are to maintain the quality and health of our planet, and also meet our growing need for energy, we will need to investigate alternative energy resources. In this next section, we are going to take a closer look at some of these possible alternatives. Many of these options are very controversial, and may have both pros and cons.

Nuclear power

Another element that is found in the crust, and which helps to meet our energy needs, is **uranium**. Uranium produces energy through the process of *nuclear fission* (chapter ??). Neutrons are aimed at the nucleii of the uranium atoms in order to split them. When the nucleus of a uranium atom is split, a large amount of energy is released as heat. This heat is used to produce steam, which turns turbines to generate electricity. Uranium is

produced as a by-product of gold in some mines in the Witwatersrand, and as a by-product in some copper mines, for example in Palaborwa. Many people regard this type of nuclear power as relatively environmentally friendly because it doesn't produce a lot of greenhouse gases. However, generating nuclear power does produce radioactive wastes, which must be carefully disposed of in order to prevent contamination. There are also concerns around leaking of nuclear materials.

Natural gas

Natural gas is formed in a similar way to oil and is often located above oil deposits in the earth's crust. 'Natural gas' refers to a hydrocarbon gas, composed mostly of methane. It is highly combustible and produces low emissions.

In June 2002, construction began on a pipeline that would stretch for 865 km between Mozambique and South Africa. Mozambique has large sources of under-utilised natural gas and so an agreement was reached between SASOL and the South African and Mozambican governments to build the pipeline, which would transport natural gas from Mozambique to South Africa. The benefits of natural gas include the fact that it is a clean-burning fossil fuel and few by-products are emitted as pollutants. It is also an economical and efficient energy source as the gas can easily be piped directly to a customer's facility.

• Biofuels

In many parts of the world, ethanol is currently being used as a substitute for crude petroleum. Ethanol can be produced through the fermentation of sugar-containing products such as sugar cane. One of the problems with this however, is the vast areas of land that are needed to cultivate the necessary crops. Crops such as maize can also be used in the process. In South Africa, a company called 'Ethanol Africa' has been set up by commercial farmers to convert their surplus maize into environmentally-friendly biofuel, and plans are underway to establish ethanol plants in some of the maize-producing provinces.

Hydropower

Hydropower produces energy from the action of falling water. As water falls from a height, the energy is used to turn turbines which produce electricity. However, for hydropower to be effective, a large dam is needed to store water. The building of a dam comes with its own set of problems such as the expense of construction, as well as the social and environmental impacts of relocating people (if the area is populated), and disrupting a natural river course.

• Solar energy

Solar energy is energy from the sun. The sun's radiation is trapped in solar panels and is then converted into electricity. While this process is environmentally friendly, and solar energy is a renewable resource, the supply of radiation is not constant (think for example of cloudy days, and nights), and the production of electricity is not efficient. Solar energy can however meet small energy needs such as the direct heating of homes.

• Geothermal energy

This type of energy comes from the natural heat below the Earth's surface. If hot underground steam can be tapped and brought to the surface, it has the potential to produce electricity.

Activity :: Discussion : Using energy wisely

The massive power cuts or 'load shedding' that South Africans began to experience at the beginning of 2008, were a dramatic wake-up call to the growing energy crisis that the country faces.

There are alternative energy sources available, but they will take years to become functional, and many of them have their own problems. Another way to look at the problem, is to put the focus on reducing how much energy is *used* rather than focusing only on ways to meet the growing demand.

- 1. In your groups, discuss ways that each of the following groups of people could save energy.
 - (a) industries
 - (b) domestic users
 - (c) farmers
- 2. Discuss creative incentives that could be used to encourage each of these groups to reduce their energy consumption.

21.11 Summary

- The **lithosphere** is the solid, outermost part of our planet and contains many important metal elements such as gold and iron, as well as products that are needed to produce energy.
- These elements are seldom found in their pure form, but rather as minerals in rocks.
- A mineral is formed through geological processes. It can either be a pure element (e.g. gold) or may consist of a number of different elements e.g. the gold-bearing mineral calaverite (AuTe₂).
- A rock is an aggregate of a number of different minerals.
- An ore is rock that contains minerals which make it valuable for mining.
- Minerals have been used throughout **history**. As new metals and minerals were discovered, important growth took place in industry, agriculture and technology.
- **Gold** is one of the most important metals in the history of South Africa. It was the discovery of gold that led to an influx of fortune-seeking foreigners, and a growth in mining villages and towns.
- Most of South Africa's gold is concentrated in the 'Golden Arc' in the area between Johannesburg and Welkom.
- Three methods are used to obtain gold from the lithosphere: **panning**, **open cast mining** and **shaft mining**.
- Gold ore must be processed so that the metal can be removed. One way to process the ore after it has been crushed is a method called **gold cyanidation**. A cyanide solution is added to the crushed ore so that a gold-cyanide solution is formed. Zinc is then added to this solution so that the gold is precipitated out.
- Gold has a number of important characteristics which make it a useful metal for jewelery and other applications. The metal is shiny, durable, malleable, ductile, is a good conductor of electricity and is also a good heat reflector.
- Gold mining has a number of environmental impacts, which include resource consumption, air pollution, poisoned water, solid waste and the destruction of biodiversity in natural areas.
- Mine rehabilitation is one way of restoring old mine sites to what they were like before.
- Iron is another important metal and is used in industry, furniture and building materials.
- Iron is usually found in minerals such as **iron oxides**. These minerals must be processed to remove the metal.
- When iron ore is **processed**, a blast furnace is used. The iron ore, carbon and a flux are added to the top of the furnace and hot air is blasted into the bottom of the furnace. A number of reactions occur in the furnace to finally remove the iron from its ore. Iron oxides are reduced by carbon monoxide to produce iron.

- Iron can occur in a number of forms, depending on its level of purity and carbon content. It can also occur in an **alloy** e.g. steel.
- Phosphates are found in sedimentary rock, which must be quarried to access the ore.
- Phosphates react with phosphoric acid or sulfuric acid to produce a superphosphate (Ca(H₂PO₄)₂), which is an important component in fertilisers.
- The products of the lithosphere are also important in meeting energy needs. Coal and oil can be extracted from the lithosphere for this purpose.
- Coal and oil are both fossil fuels. A fossil fuel is a hydrocarbon that has been formed from the fossilsed remains of plants and animals that have been under conditions of high heat and pressure over a long period of time.
- Coal and oil are non-renewable resources, meaning that once they have been used up, no more can be produced.
- Coal can be removed from the ground using strip mining, open cast mining or underground mining.
- Coal is burned to produce energy, which can be used to generate **electricity**. Coal can also be used to produce **liquid fuels** or a **syngas** which can be converted into other useful products for the chemical industry.
- Some of the environmental impacts associated with coal mining include landscape scars, spontaneous combustion, acid formation and global warming.
- Oil is also a fossil fuel but it forms in the **oceans**. It can extracted using either **pumping** or **drilling**, depending on the pressure of the oil.
- Fractional distillation of oil can be used to make products such as diesel, gasoline and liquid petroleum gas.
- Cracking can be used to convert heavy hydrocarbons to light hydrocarbons.
- The environmental impacts of oil extraction and use are similar to those for coal.
- In view of the number of environmental impacts associated with the extraction and use of coal and oil, other **alternative energy sources** should be considered. These include nuclear power, biofuels, hydropower and a number of others. All of these alternatives have their own advantages and disadvantages.

Exercise: Summary Exercise

- 1. Give one word to describe each of the following phrases:
 - (a) earth's crust together with the upper layer of the mantle
 - (b) a mineral containing silica and oxygen
 - (c) an alloy of iron and tin
 - (d) a manual technique used to sort gold from other sediments
- 2. For each of the following questions, choose the *one correct answer* from the list provided.
 - (a) One of the main reasons that South Africa's gold industry has been so economically viable is that...
 - i. gold panning can be used as an additional method to extract gold
 - ii. open cast mining can be used to extract gold reserves
 - iii. South Africa's geological history is such that its gold reserves are concentrated in large reefs
 - iv. South Africa has large amounts of water to use in mining
 - (b) The complete list of reactants in an iron blast furnace is...
- i. carbon and oxygen
- ii. coal, oxygen, iron ore and limestone
- iii. carbon, oxygen and iron ore
- iv. coal, air, iron ore and slag

3. More profits, more poisons

In the last three decades, gold miners have made use of *cyanidation* to recover gold from the ore. Over 99% of gold from ore can be extracted in this way. It allows miners to obtain gold flakes - too small for the eye to see. Gold can also be extracted from the waste of old operations which sometimes leave as much as a third of the gold behind.

The left-over cyanide can be re-used, but is more often stored in a pond behind a dam or even dumped directly into a local river. A teaspoonful of 2% solution of cyanide can kill a human adult.

Mining companies insist that cyanide breaks down when exposed to sunlight and oxygen which render it harmless. They also point to scientific studies that show that cyanide swallowed by fish will not 'bio-accumulate', which means it does not pose a risk to anyone who eats the fish. In practice, cyanide solution that seeps into the ground will not break down because of the absence of sunlight. If the cyanide solution is very acidic, it could turn into cyanide gas, which is toxic to fish. On the other hand, if the solution is alkaline the cyanide does not break down.

There are no reported cases of human death from cyanide spills. If you don't see corpses, everything is okay.

- (a) What is *cyanidation*?
- (b) What type of chemical reaction takes place during this process: precipitation, acid-base or redox?
- (c) Is the pH of the solution after cyanidation greater than, less than or equal to 7?
- (d) How is solid gold recovered from this solution?
- (e) Refer to cyanidation and discuss the meaning of the heading of this extract: *More profits, more poisons.* (DoE Grade 11 Paper 2, 2007)

Chapter 22

The Atmosphere - Grade 11

Our earth is truly an amazing planet! Not only is it exactly the right distance from the sun to have temperatures that will support life, but it is also one of the only planets to have liquid water on its surface. In addition, our earth has an atmosphere that has just the right composition to allow life to exist. The **atmosphere** is the layer of gases that surrounds the earth. We may not always be aware of them, but without these gases, life on earth would definitely not be possible. The atmosphere provides the gases that animals and plants need for respiration (breathing) and photosynthesis (the production of food), it helps to keep temperatures on earth constant and also protects us from the sun's harmful radiation.

In this chapter, we are going to take a closer look at the chemistry of the earth's atmosphere and at some of the human activities that threaten the delicate balance that exists in this part of our planet.

22.1 The composition of the atmosphere

Earth's atmosphere is a mixture of gases. Two important gases are nitrogen and oxygen, which make up about 78.1% and 20.9% of the atmosphere respectively. A third gas, Argon, contributes about 0.9%, and a number of other gases such as carbon dioxide, methane, water vapour, helium and ozone make up the remaining 0.1%. In an earlier chapter, we discussed the importance of nitrogen as a component of proteins, the building blocks of life. Similarly, oxygen is essential for life because it is the gas we need for respiration. We will discuss the importance of some of the other gases later in this chapter.



The earth's early atmosphere was very different from what it is today. When the earth formed around 4.5 billion years ago, there was probably no atmosphere. Some scientists believe that the earliest atmosphere contained gases such as water vapour, carbon dioxide, nitrogen and sulfur which were released from inside the planet as a result of volcanic activity. Many scientists also believe that the first stage in the evolution of life, around 4 billion years ago, needed an oxygen-free environment. At a later stage, these primitive forms of plant life began to release small amounts of oxygen into the atmosphere as a product of photosynthesis. During photosynthesis, plants use carbon dioxide, water and sunlight to produce simple sugars. Oxygen is also released in the process.

 $6CO_2 + 6H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6O_2$

This build-up of oxygen in the atmosphere eventually led to the formation of the ozone layer, which helped to filter the sun's harmful UV radiation so that plants were able to flourish

in different environments. As plants became more widespread and photosythesis increased, so did the production of oxygen. The increase in the amount of oxygen in the atmosphere would have allowed more forms of life to exist.

If you have ever had to climb to a very high altitude (altitude means the 'height' in the atmosphere), you will have noticed that it becomes very difficult to breathe, and many climbers suffer from 'altitude sickness' before they reach their destination. This is because the density of gases becomes less as you move higher in the atmosphere. It is **gravity** that holds the atmosphere close to the earth. As you move higher, this force weakens slightly and so the gas particles become more spread out. In effect, when you are at a high altitude, the gases in the atmosphere haven't changed, but there are fewer oxygen molecules in the same amount of air that you are able to breathe.



Definition: Earth's atmosphere

The Earth's atmosphere is a layer of gases that surround the planet, and which are held there by the Earth's gravity. The atmosphere contains roughly 78.1% nitrogen, 20.9% oxygen, 0.9% argon, 0.038% carbon dioxide, trace amounts of other gases, and a variable amount of water vapour. This mixture of gases is commonly known as air. The atmosphere protects life on Earth by absorbing ultraviolet solar radiation and reducing temperature extremes between day and night.

22.2 The structure of the atmosphere

The earth's atmosphere is divided into different layers, each with its own particular characteristics (figure 22.1).

22.2.1 The troposphere

The **troposphere** is the lowest level in the atmosphere, and it is the part in which we live. The troposphere varies in thickness, and extends from the ground to a height of about 7km at the poles and about 18km at the equator. An important characteristic of the troposphere is that its temperature *decreases* with an increase in altitude. In other words, as you climb higher, it will get colder. You will have noticed this if you have climbed a mountain, or if you have moved from a city at a high altitude to one which is lower; the average temperature is often lower where the altitude is higher. This is because the troposphere is heated from the 'bottom up'. In other words, places that are closer to the Earth's surface will be warmer than those at higher altitudes. The heating of the atmosphere will be discussed in more detail later in this chapter.

The word troposphere comes from the Greek *tropos*, meaning *turning* or *mixing*. The troposphere is the most turbulent part of the atmosphere and is the part where our **weather** takes place. Weather is the state of the air at a particular place and time e.g. if it is warm or cold, wet or dry, and how cloudy or windy it is. Generally, jet aircraft fly just above the troposphere to avoid all this turbulence.

22.2.2 The stratosphere

Above the troposphere is another layer called the **stratosphere**, where most long distance aircraft fly. The stratosphere extends from altitudes of 10 to 50km. If you have ever been in an aeroplane and have looked out the window once you are well into the flight, you will have noticed



Figure 22.1: A generalised diagram showing the structure of the atmosphere to a height of 110 $\,\rm km$

that you are actually flying above the level of the clouds. As we have already mentioned, clouds and weather occur in the troposphere, whereas the stratosphere has very stable atmospheric conditions and very little turbulence. It is easy to understand why aircraft choose to fly here!

The stratosphere is different from the troposphere because its temperature *increases* as altitude increases. This is because the stratosphere absorbs solar radiation directly, meaning that the upper layers closer to the sun will be warmer. The upper layers of the stratosphere are also warmer because of the presence of the **ozone layer**. Ozone (O_3) is formed when solar radiation splits an oxygen molecule (O_2) into two atoms of oxygen. Each individual atom is then able to combine with an oxygen molecule to form ozone. The two reactions are shown below:

$$O_2 \rightarrow O + O$$

 $O + O_2 \rightarrow O_3$

The change from one type of molecule to another produces energy, and this contributes to higher temperatures in the upper part of the stratosphere. An important function of the ozone layer is to absorb UV radiation and reduce the amount of harmful radiation that reaches the Earth's surface.



Extension: CFCs and the ozone layer

You may have heard people talking about 'the hole in the ozone layer'. What do they mean by this and do we need to be worried about it?

Most of the earth's ozone is found in the stratosphere and this limits the amount of UV radiation that reaches the earth. However, human activities have once again disrupted the chemistry of the atmosphere. Chlorofluorocarbons (CFC's) are compounds found in aerosol cans, fridges and airconditioners. In aerosol cans, it is the CFC's that cause the substance to be sprayed outwards. The bad side of CFC's is that, when they are released into the atmosphere, they break down ozone molecules so that the ozone is no longer able to protect us as much from UV rays. The 'ozone hole' is actually a thinning of the ozone layer approximately above Antarctica. Let's take a closer look at the chemical reactions that are involved in breaking down ozone:

1. When CFC's react with UV radiation, a carbon-chlorine bond in the chlorofluorocarbon breaks and a new compound is formed, with a chlorine atom.

$$CFCl_3 + UV \rightarrow CFCl_2 + Cl$$

2. The single chlorine atom reacts with ozone to form a molecule of chlorine monoxide and oxygen gas. In the process, ozone is destroyed.

$$Cl + O_3 \rightarrow ClO + O_2$$

3. The chlorine monoxide then reacts with a free oxygen atom (UV radiation breaks O_2 down into single oxygen atoms) to form oxygen gas and a single chlorine atom.

$$ClO + O \rightarrow Cl + O_2$$

4. The chlorine atom is then free to attack more ozone molecules, and the process continues. A single CFC molecule can destroy 100 000 ozone molecules.

One possible consequence of ozone depletion is an increase in the incidence of skin cancer because there is more UV radiation reaching earth's surface. CFC replacements are now being used to reduce emissions, and scientists are trying to find ways to restore ozone levels in the atmosphere.

22.2.3 The mesosphere

The mesosphere is located about 50-80/85km above Earth's surface. Within this layer, temperature decreases with increasing altitude. Temperatures in the upper mesosphere can fall as low as -100° C in some areas. Millions of meteors burn up daily in the mesosphere because of collisions with the gas particles that are present in this layer. This leads to a high concentration of iron and other metal atoms.

22.2.4 The thermosphere

The thermosphere exists at altitudes above 80 km. In this part of the atmosphere, ultraviolet (UV) and shorter X-Ray radiation from the sun cause neutral gas atoms to be *ionised*. At these radiation frequencies, photons from the solar radiation are able to dislodge electrons from neutral atoms and molecules during a collision. A *plasma* is formed, which consists of negative free electrons and positive ions. This part of the atmosphere is called the **ionosphere**. At the same time that ionisation takes place however, an opposing process called recombination also begins. Some of the free electrons are drawn to the positive ions, and combine again with them if they are in close enough contact. Since the gas density increases at lower altitudes, the recombination process occurs more often here because the gas molecules and ions are closer together. The

ionisation process produces energy which means that the upper parts of the thermosphere, which are dominated by ionisation, have a higher temperature than the lower layers where recombination takes place. Overall, temperature in the thermosphere increases with an increase in altitude.



Extension: The ionosphere and radio waves

The ionosphere is of practical importance because it allows **radio waves** to be transmitted. A radio wave is a type of electromagnetic radiation that humans use to transmit information without wires. When using high-frequency bands, the ionosphere is used to reflect the transmitted radio beam. When a radio wave reaches the ionosphere, the electric field in the wave forces the electrons in the ionosphere into oscillation at the same frequency as the radio wave. Some of the radio wave energy is given up to this mechanical oscillation. The oscillating electron will then either recombine with a positive ion, or will re-radiate the original wave energy back downward again. The beam returns to the Earth's surface, and may then be reflected back into the ionosphere for a second bounce.



The ionosphere is also home to the **auroras**. Auroras are caused by the collision of charged particles (e.g. electrons) with atoms in the earth's upper atmosphere. Charged particles are energised and so, when they collide with atoms, the atoms also become energised. Shortly afterwards, the atoms emit the energy they have gained, as light. Often these emissions are from oxygen atoms, resulting in a greenish glow (wavelength 557.7 nm) and, at lower energy levels or higher altitudes, a dark red glow (wavelength 630 nm). Many other colours can also be observed. For example, emissions from atomic nitrogen are blue, and emissions from molecular nitrogen are purple. Auroras emit visible light (as described above), and also infra-red, ultraviolet and x-rays, which can be observed from space.

Exercise: The composition of the atmosphere

1. Complete the following summary table by providing the missing information for each layer in the atmosphere.

Atmospheric	Height (km)	Gas composition	General charac-
layer			teristics
Troposphere	0-18		Turbulent; part of atmosphere where weather occurs
			Ozone reduces harmful radiation reaching Earth
Mesosphere			High concen- tration of metal atoms
	more than 80 km		

2. Use your knowledge of the atmosphere to explain the following statements:

- (a) Athletes who live in coastal areas need to acclimatise if they are competing at high altitudes.
- (b) Higher incidences of skin cancer have been recorded in areas where the ozone layer in the atmosphere is thin.
- (c) During a flight, turbulence generally decreases above a certain altitude.

22.3 Greenhouse gases and global warming

22.3.1 The heating of the atmosphere

As we mentioned earlier, the distance of the earth from the sun is not the only reason that temperatures on earth are within a range that is suitable to support life. The composition of the atmosphere is also critically important.

The earth receives electromagnetic energy from the sun in the *visible spectrum*. There are also small amounts of infrared and ultraviolet radiation in this incoming solar energy. Most of the radiation is *shortwave* radiation, and it passes easily through the atmosphere towards the earth's surface, with some being reflected before reaching the surface. At the surface, some of the energy is absorbed, and this heats up the earth's surface. But the situation is a little more complex than this.

A large amount of the sun's energy is re-radiated from the surface back into the atmosphere as **infrared** radiation, which is invisible. As this radiation passes through the atmosphere, some of it is absorbed by **greenhouse gases** such as carbon dioxide, water vapour and methane. These gases are very important because they re-emit the energy back towards the surface. By doing this, they help to warm the lower layers of the atmosphere even further. It is this 're-emission' of heat by greenhouse gases, combined with surface heating and other processes (e.g. conduction and advection) that maintain temperatures at exactly the right level to support life. Without the presence of greenhouse gases, most of the sun's energy would be lost and the Earth would be a lot colder than it is! A simplified diagram of the heating of the atmosphere is shown in figure 22.2.

22.3.2 The greenhouse gases and global warming

Many of the greenhouse gases occur naturally in small quantities in the atmosphere. However, human activities have greatly increased their concentration, and this has led to a lot of concern about the impact that this could have in *increasing* global temperatures. This phenomenon is known as **global warming**. Because the natural concentrations of these gases are low, even a small increase in their concentration as a result of human emissions, could have a big effect on temperature. But before we go on, let's look at where some of these human gas emissions come from.

• Carbon dioxide (CO₂)

Carbon dioxide enters the atmosphere through the burning of fossil fuels (oil, natural gas, and coal), solid waste, trees and wood products, and also as a result of other chemical reactions (e.g. the manufacture of cement). Carbon dioxide can also be *removed* from the atmosphere when it is absorbed by plants during photosynthesis.

• Methane (CH₄)

Methane is emitted when coal, natural gas and oil are produced and transported. Methane emissions can also come from livestock and other agricultural practices and from the decay of organic waste.



Figure 22.2: The heating of the Earth's atmosphere

• Nitrous oxide (N₂O)

Nitrous oxide is emitted by agriculture and industry, and when fossil fuels and solid waste are burned.

• Fluorinated gases (e.g. hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride)

These gases are all *synthetic*, in other words they are man-made. They are emitted from a variety of industrial processes. Fluorinated gases are sometimes used in the place of other ozone-depleting substances (e.g. CFC's). These are very powerful greenhouse gases, and are sometimes referred to as High Global Warming Potential gases ('High GWP gases').

Overpopulation is a major problem in reducing greenhouse gas emissions, and in slowing down global warming. As populations grow, their demands on resources (e.g. energy) increase, and so does their production of greenhouse gases.



Extension: Ice core drilling - Taking a look at earth's past climate

Global warming is a very controversial issue. While many people are convinced that the increase in average global temperatures is directly related to the increase in atmospheric concentrations of carbon dioxide, others argue that the climatic changes we are seeing are part of a natural pattern. One way in which scientists are able to understand what is happening at present, is to understand the earth's *past* atmosphere, and the factors that affected its temperature.

So how, you may be asking, do we know what the earth's *past* climate was like? One method that is used is **ice core drilling**. Antarctica is the coldest continent on earth, and because of this there is very little melting that takes place. Over thousands of years, ice has accumulated in layers and has become more and more compacted as new ice is added. This is partly why Antarctica is also on average one of the *highest* continents! On average, the ice sheet that covers Antarctica is 2500 m thick, and at its deepest location, is 4700 m thick.

As the snow is deposited on top of the ice sheet each year, it traps different chemicals and impurities which are dissolved in the ice. The ice and impurities hold information about the Earth's environment and climate at the time that the ice was deposited. Drilling an ice core from the surface down, is like taking a journey back in time. The deeper into the ice you venture, the older the layer of ice. By analysing the gases and oxygen isotopes that are present (along with many other techniques) in the ice at various points in the earth's history, scientists can start to piece together a picture of what the earth's climate must have been like.



One of the most well known ice cores was the one drilled at a Russian station called Vostok in central Antarctica. So far, data has been gathered for dates as far back as 160 000 years!

Activity :: Case Study : Looking at past climatic trends

Make sure that you have read the 'Information box' on ice core drilling before you try this activity.

The values in the table below were extrapolated from data obtained by scientists studying the Vostok ice core. 'Local temperature change' means by how much the temperature at that time was different from what it is today. For example, if the local temperature change 160 000 years ago was -9°C, this means that atmospheric temperatures at that time were $9^{\circ}C$ lower than what they are today. 'ppm' means 'parts per million' and is a unit of measurement for gas concentrations. $\frac{428}{428}$

Years before present	Local temperature	Carbon
(× 1000)	change (°C)	dioxide
		(ppm)
160	-9	190
150	-10	205
140	-10	240
130	-3	280
120	+1	278
110	-4	240
100	-8	225
90	-5	230
80	-6	220
70	-8	250
60	-9	190
50	-7	220
40	-8	180
30	-7	225
20	-9	200
10	-2	260
0 (1850)	-0.5	280
Present		371

Questions

- On the same set of axes, draw graphs to show how temperature and carbon dioxide concentrations have changed over the last 160 000 years. Hint: 'Years before present' will go on the x-axis, and should be given *negative* values.
- 2. Compare the graphs that you have drawn. What do you notice?
- 3. Is there a relationship between temperature and the atmospheric concentration of carbon dioxide?
- 4. Do these graphs *prove* that temperature changes are determined by the concentration of gases such as carbon dioxide in the atmosphere? Explain your answer.
- 5. What other factors might you need to consider when analysing climatic trends?

22.3.3 The consequences of global warming

Activity :: Group Discussion : The impacts of global warming

In groups of 3-4, read the following extracts and then answer the questions that follow.

By 2050 Warming to Doom Million Species, Study Says

By 2050, rising temperatures exacerbated by human-induced belches of carbon dioxide and other greenhouse gases could send more than a million of Earth's land-dwelling plants and animals down the road to extinction, according to a recent study. "Climate change now represents at least as great a threat to the number of species surviving on Earth as habitat-destruction and modification," said Chris Thomas, a conservation biologist at the University of Leeds in the United Kingdom.

The researchers worked independently in six biodiversity-rich regions around the world, from Australia to South Africa, plugging field data on species distribution and regional climate into computer models that simulated the ways species' ranges are expected to move in response to temperature and climate changes. According to the researchers' collective results, the predicted range of climate change by 2050 will place 15 to 35 percent of the 1 103 species studied at risk of extinction.

National Geographic News, 12 July 2004

Global Warming May Dry Up Africa's Rivers, Study Suggests

Many climate scientists already predict that less rain will fall annually in parts of Africa within 50 years due to global warming. Now new research suggests that even a small decrease in rainfall on the continent could cause a drastic reduction in river water, the lifeblood for rural populations in Africa.

A decrease in water availability could occur across about 25 percent of the continent, according to the new study. Hardest hit would be areas in northwestern and southern Africa, with some of the most serious effects striking large areas of Botswana and South Africa.

To predict future rainfall, the scientists compared 21 of what they consider to be the best climate change models developed by research teams around the world. On average, the models forecast a 10 to 20% drop in rainfall in northwestern and southern Africa by 2070. With a 20% decrease, Cape Town would be left with just 42% of its river water, and "Botswana would completely dry up," de Wit said. In parts of northern Africa, river water levels would drop below 50%.

Less river water would have serious implications not just for people but for the many animal species whose habitats rely on regular water supplies. *National Geographic News, 3 March 2006*

Discussion questions

- 1. What is meant by 'biodiversity'?
- 2. Explain why global warming is likely to cause a loss of biodiversity.
- 3. Why do you think a loss of biodiversity is of such concern to conservationists?
- 4. Suggest some plant or animal species in South Africa that you think might be particularly vulnerable to extinction if temperatures were to rise significantly. Explain why you chose these species.
- 5. In what way do people, animals and plants rely on river water?
- 6. What effect do you think a 50% drop in river water level in some parts of Africa would have on the people living in these countries?
- 7. Discuss some of the other likely impacts of global warming that we can expect (e.g. sea level rise, melting of polar ice caps, changes in ocean currents).

22.3.4 Taking action to combat global warming

Global warming is a major concern at present. A number of organisations, panels and research bodies have been working to gather accurate and relevant information so that a true picture of our current situation can be painted. One important orgaisation that you may have heard of is the **Intergovernmental Panel on Climate Change** (IPCC). The IPCC was established in 1988 by two United Nations organizations, the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP), to evaluate the risk of climate change brought on by humans. You may also have heard of the **Kyoto Protocol**, which will be discussed a little later.

Activity :: Group Discussion : World carbon dioxide emissions

The data in the table below shows carbon dioxide emissions from the consumption of fossil fuels (in million metric tons of carbon dioxide).

Region or Country	1980	1985	1990	1995	2000	2004
United States	4754	4585	5013	5292	5815	5912
Brazil	186	187	222	288	345	336
France	487	394	368	372	399	405
UK	608	588	598	555	551	579
Saudi Arabia	175	179	207	233	288	365
Botswana	1.26	1.45	2.68	3.44	4.16	3.83
South Africa	234	298	295	344	378	429
India	299	439	588	867	1000	1112
World Total	18333	19412	21426	22033	23851	27043

Questions

- 1. Using a coloured pen, highlight those countries that are 'developed' and those that are 'developing'.
- Explain why CO₂ emissions are so much higher in developed countries than in developing countries.
- 3. How does South Africa compare to the other developing countries, and also to the developed countries?

Carbon dioxide emissions are a major problem worldwide. The **Kyoto Protocol** was signed in Kyoto, Japan in December 1997. Its main objective was to reduce global greenhouse gas emissions by encouraging countries to become signatories to the guidelines that had been laid out in the protocol. These guidelines set targets for the world's major producers to reduce their emissions within a certain time. However, some of the worst contributors to greenhouse gas emissions (e.g. USA) were not prepared to sign the protocol, partly because of the potential effect this would have on the country's economy, which relies on industry and other 'high emission' activities.

Panel discussion

Form groups with 5 people in each. Each person in the group must adopt one of the following roles during the discussion:

- the owner of a large industry
- an environmental scientist
- an economist
- a politician
- a chairperson for the discussion

In your group, you are going to discuss some of the economic and environmental implications for a country that decides to sign the Kyoto Protocol. Each person will have the opportunity to express the view of the character they have adopted. You may ask questions of the other people, or challenge their ideas, provided that you ask permission from the chairperson first.

22.4 Summary

- The **atmosphere** is the layer of gases that surrounds Earth. These gases are important in sustaining life, regulating temperature and protecting Earth from harmful radiation.
- The gases that make up the atmosphere are nitrogen, oxygen, carbon dioxide and others e.g. water vapour, methane.
- There are four layer in the atmosphere, each with their own characteristics.

- The **troposphere** is the lowest layer and here, temperature decreases with an increase in altitude. The troposphere is where weather occurs.
- The next layer is the **stratosphere** where temperature increases with an increase in altitude because of the presence of ozone in this layer, and the direct heating from the sun.
- The depletion of the ozone layer is largely because of CFC's, which break down ozone through a series of chemical reactions.
- The **mesosphere** is characterised by very cold temperatures and meteor collisions. The mesosphere contains high concentrations of metal atoms.
- In the **thermosphere**, neutral atoms are ionised by UV and X-ray radiation from the sun. Temperature increases with an increase in altitude because of the energy that is released during this ionisation process, which occurs mostly in the upper thermosphere.
- The thermosphere is also known as the **ionosphere**, and is the part of the atmosphere where radio waves can be transmitted.
- The **auroras** are bright coloured skies that occur when charged particles collide with atoms in the upper atmosphere. Depending on the type of atom, energy is released as light at different wavelengths.
- The Earth is heated by radiation from the sun. Incoming radiation has a short wavelength and some is absorbed directly by the Earth's surface. However, a large amount of energy is re-radiated as longwave infrared radiation.
- Greenhouse gases such as carbon dioxide, water vapour and methane absorb infrared radiation and re-emit it back towards the Earth's surface. In this way, the bottom layers of the atmsophere are kept much warmer than they would be if all the infrared radiation was lost.
- Human activities such as the burning of fossil fuels, increase the concentration of greenhouse gases in the atmosphere and may contribute towards **global warming**.
- Some of the impacts of global warming include changing climate patterns, rising sea levels and a loss of biodiversity, to name a few. Interventions are needed to reduce this phenomenon.



Exercise: Summary Exercise

1. The atmosphere is a relatively thin layer of gases which support life and provide protection to living organisms. The force of gravity holds the atmosphere against the earth. The diagram below shows the temperatures associated with the various layers that make up the atmosphere and the altitude (height) from the earth's surface.



- (a) Write down the names of the layers A, B and D of the atmosphere.
- (b) In which one of the layers of the atmosphere is ozone found?
- (c) Give an explanation for the decrease in temperature as altitude increases in layer A.
- (d) In layer B, there is a steady increase in temperature as the altitude increases. Write down an explanation for this trend.

2. Planet Earth in Danger

It is now accepted that greenhouse gases are to blame for planet earth getting warmer. The increase in the number of sudden floods in Asia and droughts in Africa; the rising sea level and increasing average temperatures are global concerns. Without natural greenhouse gases,like carbon dioxide and water vapour,life on earth is not possible. However, the increase in levels of carbon dioxide in the atmosphere since the Industrial Revolution is of great concern. Greater disasters are to come, which will create millions of climate refugees. It is our duty to take action for the sake of future generations who will pay dearly for the wait-and-see attitude of the current generation. Urgent action to reduce waste is needed. Global warming is a global challenge and calls for a global response now, not later.

(Adapted from a speech by the French President, Jacques Chirac)

- (a) How do greenhouse gases, such as carbon dioxide, heat up the earth's surface?
- (b) Draw a Lewis structure for the carbon dioxide molecule
- (c) The chemical bonds within the carbon dioxide molecule are polar. Support this statement by performing a calculation using the table of electronegativities.
- (d) Classify the carbon dioxide molecule as polar or non-polar. Give a reason for your answer.
- (e) Suggest ONE way in which YOU can help to reduce the emissions of greenhouse gases.
- 3. Plants need carbon dioxide (CO_2) to manufacture food. However, the engines of motor vehicles cause too much carbon dioxide to be released into the atmosphere.
 - (a) State the possible consequence of having too much carbon dioxide in the atmosphere.

(b) Explain **two** possible effects on humans if the amount of carbon dioxide in the atmosphere becomes too low.

(DoE Exemplar Paper Grade 11, 2007)

Chapter 23

The Chemical Industry - Grade 12

23.1 Introduction

The chemical industry has been around for a very long time, but not always in the way we think of it today! Dyes, perfumes, medicines and soaps are all examples of products that have been made from chemicals that are found in either plants or animals. However, it was not until the time of the Industrial Revolution that the chemical industry as we know it today began to develop. At the time of the Industrial Revolution, the human population began to grow very quickly and more and more people moved into the cities to live. With this came an increase in the need for things like paper, glass, textiles and soaps. On the farms, there was a greater demand for fertilisers to help produce enough food to feed all the people in cities and rural areas. Chemists and engineers responded to these growing needs by using their technology to produce a variety of new chemicals. This was the start of the chemical industry.

In South Africa, the key event that led to the growth of the chemical industry was the discovery of diamonds and gold in the late 1800's. Mines needed explosives so that they could reach the diamonds and gold-bearing rock, and many of the main chemical companies in South Africa developed to meet this need for explosives. In this chapter, we are going to take a closer look at one of South Africa's major chemical companies, **Sasol**, and will also explore the **chloralkali** and **fertiliser** industries.

23.2 Sasol

Oil and natural gas are important fuel resources. Unfortunately, South Africa has no large oil reserves and, until recently, had very little natural gas. One thing South Africa *does* have however, is large supplies of **coal**. Much of South Africa's chemical industry has developed because of the need to produce oil and gas from coal, and this is where Sasol has played a very important role.

Sasol was established in 1950, with its main aim being to convert low grade coal into petroleum (crude oil) products and other chemical feedstocks. A 'feedstock' is something that is used to make another product. Sasol began producing oil from coal in 1955.

Fac

The first interest in coal chemistry started as early as the 1920's. In the early 1930's a research engineer called Etienne Rousseau was employed to see whether oil could be made from coal using a new German technology called the **Fischer-Tropsch** process. After a long time, and after many negotiations, Rousseau was given the rights to operate a plant using this new process. As a result, the government-sponsored 'South African Coal, Oil and Gas Corporation Ltd'

(commonly called 'Sasol') was formed in 1950 to begin making oil from coal. A manufacturing plant was established in the Free State and the town of **Sasol-burg** developed around this plant. Production began in 1955. In 1969, the **Natref** crude oil refinery was established, and by 1980 and 1982 Sasol Two and Sasol Three had been built at **Secunda**.

23.2.1 Sasol today: Technology and production

Today, Sasol is an oil and gas company with diverse chemical interests. Sasol has three main areas of operation: Firstly, **coal to liquid fuels technology**, secondly the production of **crude oil** and thirdly the conversion of **natural gas to liquid fuel**.

1. Coal to liquid fuels

Sasol is involved in mining coal and converting it into synthetic fuels, using the **Fischer-Tropsch** technology. Figure 23.1 is a simplified diagram of the process that is involved.



Figure 23.1: The gasification of coal to produce liquid fuels

Coal gasification is also known as the **Sasol/Lurgi** gasification process, and involves converting low grade coal to a synthesis gas. Low grade coal has a low percentage carbon, and contains other impurities. The coal is put under extremely high pressure and temperature in the presence of steam and oxygen. The gas that is produced has a high concentration of hydrogen (H_2) and carbon monoxide (CO). That is why it is called a 'synthesis gas', because it is a mixture of more than one gas.

In the **Sasol Advanced Synthol (SAS) reactors**, the gas undergoes a high temperature Fischer-Tropsch conversion. Hydrogen and carbon monoxide react under high pressure and temperature and in the presence of an iron catalyst, to produce a range of hydrocarbon products. Below is the generalised equation for the process. Don't worry too much about the numbers that you see in front of the reactants and products. It is enough just to see that the reaction of hydrogen and carbon monoxide (the two gases in the *synthesis gas*) produces a hydrocarbon and water.

 $(2n+1)H_2+nCO\rightarrow C_nH_{2n+2}+nH_2O$

A range of hydrocarbons are produced, including petrol, diesel, jet fuel, propane, butane, ethylene, polypropylene, alcohols and acetic acids.

Important: Different types of fuels

It is important to understand the difference between types of fuels and the terminology that is used for them. The table below summarises some of the fuels that will be mentioned in this chapter.

Compound	Description
Petroleum	A naturally occurring liquid that forms in the earth's
(crude oil)	lithosphere (see section 21.9 in chapter 21). It is a
	mixture of hydrocarbons, mostly alkanes, ranging
	from C_5H_{12} to $C_{18}H_{38}$.
Natural gas	Natural gas has the same origin as petroleum, but
	is made up of shorter hydrocarbon chains.
Paraffin wax	This is made up of longer hydrocarbon chains, mak-
	ing it a solid compound.
Petrol (gasoline)	A liquid fuel that is derived from petroleum, but
	which contains extra additives to increase the oc-
	tane rating of the fuel. Petrol is used as a fuel in
	combustion engines.
Diesel	Diesel is also derived from petroleum, but is used in
	diesel engines.
Liquid Petroleum	LPG is a mixture of hydrocarbon gases, and is used
Gas (LPG)	as a fuel in heating appliances and vehicles. Some
	LPG mixtures contain mostly propane, while oth-
	ers are mostly butane. LPG is manufactured when
	crude oil is refined, or is extracted from natural gas
	supplies in the ground.
Paraffin	This is a technical name for the alkanes, but refers
	specifically to the <i>linear</i> alkanes. <i>Isoparaffin</i> refers
	to non-linear alkanes.
Jet fuel	A type of aviation fuel designed for use in jet engined
	aircraft. It is an oil-based fuel and contains additives
	such as antioxidants, corrosion inhibitors and icing
	inhibitors.

You will notice in the diagram that Sasol doesn't only produce liquid fuels, but also a variety of other chemical products. Sometimes it is the synthetic fuels themselves that are used as feedstocks to produce these chemical products. This is done through processes such as **hydrocracking** and **steamcracking**. Cracking is when heavy hydrocarbons are converted to simpler light hydrocarbons (e.g. LPG and petrol) through the breaking of C-C bonds. A heavy hydrocarbon is one that has a high number of hydrogen and carbon atoms (more solid), and a light hydrocarbon has fewer hydrogen and carbon atoms and is either a liquid or a gas.



Definition: Hydrocracking

Hydrocracking is a cracking process that is assisted by the presence of an elevated partial pressure of hydrogen gas. It produces chemical products such as ethane, LPG, isoparaffins, jet fuel and diesel.

23.2

Definition: Steam cracking

Steam cracking occurs under very high temperatures. During the process, a liquid or gaseous hydrocarbon is diluted with steam and then briefly heated in a furnace at a temperature of about $850^{\circ}C$. Steam cracking is used to convert *ethane* to *ethylene*. Ethylene is a chemical that is needed to make plastics. Steam cracking is also used to make propylene, which is an important fuel gas.

2. Production of crude oil

Sasol obtains crude oil off the coast of Gabon (a country in West Africa) and refines this at the Natref refinery (figure 23.2). Sasol also sells liquid fuels through a number of service stations.



Figure 23.2: Crude oil is refined at Sasol's Natref refinery to produce liquid fuels

3. Liquid fuels from natural gas

Sasol produces natural gas in Mozambique and is expanding its 'gas to fuel' technology. The gas undergoes a complex process to produce linear-chained hydrocarbons such as waxes and paraffins (figure 23.3).



Figure 23.3: Conversion of natural gas to liquid fuels

In the **autothermal reactor**, methane from natural gas reacts with steam and oxygen over an iron-based catalyst to produce a *synthesis gas*. This is a similar process to that involved in coal gasification. The oxygen is produced through the **fractional distillation of air**.

Definition: Fractional distillation

Fractional distillation is the separation of a mixture into its component parts, or fractions. Since air is made up of a number of gases (with the major component being nitrogen), fractional distillation can be used to separate it into these different parts.

The syngas is then passes through a **Sasol Slurry Phase Distillate (SSPD)** process. In this process, the gas is reacted at far lower temperatures than in the SAS reactors. Apart

from hard wax and candle wax, high quality diesel can also be produced in this process. Residual gas from the SSPD process is sold as pipeline gas while some of the lighter hydrocarbons are treated to produce kerosene and paraffin. Ammonia is also produced, which can be used to make fertilisers.



Sasol is a major player in the emerging Southern African natural gas industry, after investing 1.2 billion US dollars to develop onshore gas fields in central Mozambique. Sasol has been supplying natural gas from Mozambique's Temane field to customers in South Africa since 2004.



Exercise: Sasol processes

Refer to the diagrams summarising the three main Sasol processes, and use these to answer the following questions:

- 1. Explain what is meant by each of the following terms:
 - (a) crude oil
 - (b) hydrocarbon
 - (c) coal gasification
 - (d) synthetic fuel
 - (e) chemical feedstock
- 2. (a) What is diesel?
 - (b) Describe two ways in which diesel can be produced.
- Describe one way in which lighter chemical products such as ethylene, can be produced.
- 4. Coal and oil play an important role in Sasol's technology.
 - (a) In the table below, summarise the similarities and differences between coal, oil and natural gas in terms of how they are formed ('origin'), their general chemical formula and whether they are solid, liquid or gas.

	Coal	Oil	Natural gas
Origin			
General			
chemical			
formula			
Solid, liquid			
or gas			

- (b) In your own words, describe how coal is converted into liquid fuels.
- (c) Explain why Sasol's 'coal to liquid fuels' technology is so important in meeting South Africa's fuel needs.
- (d) Low grade coal is used to produce liquid fuels. What is the main use of higher grade coal in South Africa?

23.2

Activity :: Case Study : Safety issues and risk assessments

Safety issues are important to consider when dealing with industrial processes. Read the following extract that appeared in the Business report on 6th February 2006, and then discuss the questions that follow.

Cape Town - Sasol, the petrochemicals group, was likely to face prosecution on 10 charges of culpable homicide after an explosion at its Secunda plant in 2004 in which 10 people died, a Cape Town labour law specialist said on Friday. The specialist, who did not want to be named, was speaking after the inquiry into the explosion was concluded last Tuesday. It was convened by the labour department.

The evidence led at the inquiry showed a failure on the part of the company to conduct a proper risk assessment and that: Sasol failed to identify hazards associated with a high-pressure gas pipeline running through the plant, which had been shut for extensive maintenance work, in the presence of hundreds of people and numerous machines, including cranes, fitters, contractors, and welding and cutting machines. Because there had never been a risk assessment, the hazard of the high-pressure pipeline had never been identified.

Because Sasol had failed to identify the risk, it did not take any measures to warn people about it, mark the line or take precautions. There had also been inadequacy in planning the shutdown work. In the face of a barrage of criticism for the series of explosions that year, Sasol embarked on a comprehensive programme to improve safety at its operations and appointed Du Pont Safety Resources, the US safety consultancy, to benchmark the petrochemical giant's occupational health and safety performance against international best practice.

- 1. Explain what is meant by a 'risk assessment'.
- 2. Imagine that you have been asked to conduct a risk assessment of the Sasol/Lurgi gasification process. What information would you need to know in order to do this assessment?
- 3. In groups, discuss the importance of each of the following in ensuring the safety of workers in the chemical industry:
 - employing experienced Safety, Health and Environment personnel
 - regular training to identify hazards
 - · equipment maintenance and routine checks
- 4. What other precautions would you add to this list to make sure that working conditions are safe?

23.2.2 Sasol and the environment

From its humble beginnings in 1950, Sasol has grown to become a major contributor towards the South African economy. Today, the industry produces more than 150 000 barrels of fuels and petrochemicals per day, and meets more than 40% of South Africa's liquid fuel requirements. In total, more than 200 fuel and chemical products are manufactured at Sasolburg and Secunda, and these products are exported to over 70 countries worldwide. This huge success is largely due to Sasol's ability to diversify its product base. The industry has also helped to provide about 170 000 jobs in South Africa, and contributes around R40 billion to the country's Gross Domestic Product (GDP).

However, despite these obvious benefits, there are always environmental costs associated with industry. Apart from the vast quantities of resources that are needed in order for the industry to operate, the production process itself produces waste products and pollutants.

Exercise: Consumption of resources

Any industry will always use up huge amounts of resources in order to function effectively, and the chemical industry is no exception. In order for an industry to operate, some of the major resources that are needed are **energy** to drive many of the processes, **water**, either as a coolant or as part of a process and **land** for mining or operations.

Refer to the data table below which shows Sasol's water use between 2002 and 2005 (*Sasol Sustainable Development Report 2005*), and answer the questions that follow.

Water use $(1000m^3)$	2002	2003	2004	2005
River water	113 722	124 179	131 309	124 301
Potable water	15 126	10 552	10 176	10 753
Total	157 617	178 439	173 319	163 203

- 1. Explain what is meant by 'potable' water.
- 2. Describe the trend in Sasol's water use that you see in the above statistics.
- 3. Suggest possible reasons for this trend.
- 4. List some of the environmental impacts of using large amounts of river water for industry.
- 5. Suggest ways in which these impacts could be reduced

Exercise: Industry and the environment

Large amounts of gases and pollutants are released during production, and when the fuels themselves are used. Refer to the table below, which shows greenhouse gas and atmospheric pollution data for Sasol between 2002 and 2005, and then answer the questions that follow. (*Source: Sasol Sustainable Development Report 2005*)

Greenhouse gases and air pollutants (kilotonnes)	2002	2003	2004	2005
Carbon dioxide (CO_2)	57 476	62 873	66 838	60 925
Hydrogen sulfide (H_2S)	118	105	102	89
Nitrogen oxides (NO_x)	168	173	178	166
Sulfur dioxide (SO_2)	283	239	261	222

- 1. Draw line graphs to show how the quantity of each pollutant produced has changed between 2002 and 2005.
- 2. Describe what you see in the graphs, and suggest a reason for this trend.
- 3. Explain what is meant by each of the following terms:
 - (a) greenhouse gas
 - (b) global warming
- 4. Describe some of the possible effects of global warming.
- 5. When sulfur dioxide is present in the atmosphere, it may react with water vapour to produce weak *sulfuric acid*. In the same way, nitrogen dioxide and water vapour react to form *nitric acid*. These reactions in the atmosphere may cause **acid rain**. Outline some of the possible consequences of acid rain.
- 6. Many industries are major contributors towards environmental problems such as global warming, environmental pollution, over-use of resources and acid rain. Industries are in a difficult position: On one hand they must meet the ever increasing demands of society, and on the other, they must achieve this with as little environmental impact as possible. This is a huge challenge.

- Work in groups of 3-4 to discuss ways in which industries could be encouraged (or in some cases forced) to reduce their environmental impact.
- Elect a spokesperson for each group, who will present your ideas to the class.
- Are the ideas suggested by each group practical?
- How easy or difficult do you think it would be to implement these ideas in South Africa?



Sasol is very aware of its responsibility towards creating cleaner fuels. From 1st January 2006, the South African government enforced a law to prevent lead from being added to petrol. Sasol has complied with this. One branch of Sasol, **Sasol Technology** also has a bio-diesel research and development programme focused on developing more environmentally friendly forms of diesel. One way to do this is to use renewable resources such as soybeans to make diesel. Sasol is busy investigating this new technology.

23.3 The Chloralkali Industry

The chlorine-alkali (chloralkali) industry is an important part of the chemical industry, and produces **chlorine** and **sodium hydroxide** through the electrolysis of salt (NaCl). The main raw material is **brine** which is a saturated solution of sodium chloride (NaCl) that is obtained from natural salt deposits.

The products of this industry have a number of important uses. **Chlorine** is used to purify water, and is used as a disinfectant. It is also used in the manufacture of many every-day items such as hypochlorous acid, which is used to kill bacteria in drinking water. Chlorine is also used in paper production, antiseptics, food, insecticides, paints, petroleum products, plastics (such as polyvinyl chloride or PVC), medicines, textiles, solvents, and many other consumer products. Many chemical products such as chloroform and carbon tetrachloride also contain chlorine.

Sodium hydroxide (also known as 'caustic soda') has a number of uses, which include making soap and other cleaning agents, purifying bauxite (the ore of aluminium), making paper and making rayon (artificial silk).

23.3.1 The Industrial Production of Chlorine and Sodium Hydroxide

Chlorine and sodium hydroxide can be produced through a number of different reactions. However, one of the problems is that when chlorine and sodium hydroxide are produced together, the chlorine combines with the sodium hydroxide to form chlorate (ClO^-) and chloride (Cl^-) ions. This produces sodium chlorate, NaClO, a component of household bleach. To overcome this problem the chlorine and sodium hydroxide must be separated from each other so that they don't react. There are three industrial processes that have been designed to overcome this problem, and to produce chlorine and sodium hydroxide. All three methods involve **electrolytic cells** (chapter 17). Important: Electrolytic cells

Electrolytic cells are used to split up or loosen ions. They are made up of an **electrolyte** and two electrodes, the **cathode** and the **anode**. An electrolytic cell is activated by applying an external electrical current. This creates an electrical potential across the cathode and anode, and forces a chemical reaction to take place in the electrolyte. Cations flow towards the cathode and are reduced. Anions flow to the anode and are oxidised. Two new products are formed, one product at the cathode and one at the anode.

1. The Mercury Cell

In the mercury-cell (figure 23.4), brine passes through a chamber which has a carbon electrode (the anode) suspended from the top. Mercury flows along the floor of this chamber and acts as the cathode. When an electric current is applied to the circuit, chloride ions in the electrolyte are oxidised to form chlorine gas.

$$2\mathrm{Cl}^-_{\mathrm{(aq)}} \to \mathrm{Cl}_{2\mathrm{(g)}} + 2\mathrm{e}^-$$

At the cathode, sodium ions are reduced to sodium.

$$2Na^+_{(aq)} + 2e^- \rightarrow 2Na_{(Hg)}$$

The sodium dissolves in the mercury, forming an amalgam of sodium and mercury. The amalgam is then poured into a separate vessel, where it decomposes into sodium and mercury. The sodium reacts with water in the vessel and produces sodium hydroxide (caustic soda) and hydrogen gas, while the mercury returns to the electrolytic cell to be used again.

$$2Na_{(Hg)} + 2H_2O_{(1)} \rightarrow 2NaOH_{(ag)} + H_{2(g)}$$



Figure 23.4: The Mercury Cell

This method, however, only produces a fraction of the chlorine and sodium hydroxide that is used by industry as it has certain disadvantages: mercury is expensive and toxic, and although it is returned to the electrolytic cell, some always escapes with the brine that has been used. The mercury reacts with the brine to form mercury(II) chloride. In the past this effluent was released into lakes and rivers, causing mercury to accumulate in fish and other animals feeding on the fish. Today, the brine is treated before it is discharged so that the environmental impact is lower.

2. The Diaphragm Cell

In the diaphragm-cell (figure 23.5), a porous diaphragm divides the electrolytic cell, which contains brine, into an anode compartment and a cathode compartment. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment. When an electric current passes through the brine, the salt's chlorine ions and sodium ions move to the electrodes. Chlorine gas is produced at the anode. At the cathode, sodium ions react with water, forming caustic soda and hydrogen gas. Some salt remains in the solution with the caustic soda and can be removed at a later stage.



Figure 23.5: Diaphragm Cell

This method uses less energy than the mercury cell, but the sodium hydroxide is not as easily concentrated and precipitated into a useful substance.



To separate the chlorine from the sodium hydroxide, the two half-cells were traditionally separated by a porous asbestos diaphragm, which needed to be replaced every two months. This was damaging to the environment, as large quantities of asbestos had to be disposed. Today, the asbestos is being replaced by other polymers which do not need to be replaced as often.

3. The Membrane Cell

The membrane cell (figure 23.6) is very similar to the diaphragm cell, and the same reactions occur. The main difference is that the two electrodes are separated by an ion-selective membrane, rather than by a diaphragm. The structure of the membrane is such that it allows cations to pass through it between compartments of the cell. It does not allow anions to pass through. This has nothing to do with the size of the pores, but rather with the charge on the ions. Brine is pumped into the anode compartment, and only the positively charged sodium ions pass into the cathode compartment, which contains pure water.

At the positively charged anode, Cl^- ions from the brine are oxidised to Cl_2 gas.

$$2\text{Cl}^- \rightarrow \text{Cl}_{2(g)} + 2e^-$$

At the negatively charged cathode, hydrogen ions in the water are reduced to hydrogen gas.



Figure 23.6: Membrane Cell

$$2\mathrm{H}^+_{(\mathrm{aq})} + 2\mathrm{e}^- \rightarrow \mathrm{H}_{2(\mathrm{g})}$$

The Na^+ ions flow through the membrane to the cathode compartment and react with the remaining hydroxide (OH^-) ions from the water to form sodium hydroxide (NaOH). The chloride ions cannot pass through, so the chlorine does not come into contact with the sodium hydroxide in the cathode compartment. The sodium hydroxide is removed from the cell. The overall equation is as follows:

 $2NaCl+2H_20\rightarrow Cl_2+H_2+2NaOH$

The advantage of using this method is that the sodium hydroxide that is produced is very pure because it is kept separate from the sodium chloride solution. The caustic soda therefore has very little salt contamination. The process also uses less electricity and is cheaper to operate.



Exercise: The Chloralkali industry

1. Refer to the flow diagram below which shows the reactions that take place in the membrane cell, and then answer the questions that follow.



- (a) What liquid is present in the cathode compartment at (a)?
- (b) Identify the gas that is produced at (b).
- (c) Explain one feature of this cell that allows the Na^+ and OH^- ions to react at (c).
- (d) Give a balanced equation for the reaction that takes place at (c).
- 2. Summarise what you have learnt about the three types of cells in the chloralkali industry by completing the table below:

	Mercury cell	Diaphragm	Membrane
		cell	cell
Main raw material			
Mechanism of sep-			
arating Cl_2 and			
NaOH			
Anode reaction			
Cathode reaction			
Purity of NaOH pro-			
duced			
Energy consumption			
Environmental			
impact			

23.3.2 Soaps and Detergents

Another important part of the chloralkali industry is the production of **soaps** and **detergents**. You will remember from an earlier chapter, that water has the property of *surface tension*. This means that it tends to bead up on surfaces and this slows down the wetting process and makes cleaning difficult. You can observe this property of surface tension when a drop of water falls onto a table surface. The drop holds its shape and does not spread. When cleaning, this surface tension must be reduced so that the water can spread. Chemicals that are able to do this are called **surfactants**. Surfactants also loosen, disperse and hold particles in suspension, all of which are an important part of the cleaning process. Soap is an example of one of these surfactants. Detergents contain one or more surfactants. We will go on to look at these in more detail.



Definition: Surfactant

A surfactant is a wetting agent that lowers the surface tension of a liquid, allowing it to spread more easily.

1. Soaps

In chapter 10, a number of important biological macromolecules were discussed, including carbohydrates, proteins and nucleic acids. **Fats** are also biological macromolecules. A fat is made up of an alcohol called glycerol, attached to three fatty acids (figure 23.7). Each **fatty acid** is made up of a carboxylic acid attached to a long hydrocarbon chain. An **oil** has the same structure as a fat, but is a liquid rather than a solid. Oils are found in plants (e.g. olive oil, sunflower oil) and fats are found in animals.



Figure 23.7: The structure of a fat, composed of an alcohol and three fatty acids

To make soap, sodium hydroxide (NaOH) or potassium hydroxide (KOH) must be added to a fat or an oil. During this reaction, the glycerol is separated from the hydrocarbon chain in the fat, and is replaced by either potassium or sodium ions (figure 23.8). Soaps are the water-soluble sodium or potassium salts of fatty acids.



Soaps can be made from either fats or oils. Beef fat is a common source of fat, and vegetable oils such as palm oil are also commonly used.

Fatty acids consist of two parts: a carboxylic acid group and a hydrocarbon chain. The hydrocarbon chain is *hydrophobic*, meaning that it is repelled by water. However, it is attracted to grease, oils and other dirt. The carboxylic acid is *hydrophilic*, meaning that it is attracted to water. Let's imagine that we have added soap to water in order to clean a dirty rugby jersey. The hydrocarbon chain will attach itself to the soil particles in the



Figure 23.8: Sodium hydroxide reacts with a fat to produce glycerol and sodium salts of the fatty acids

jersey, while the carboxylic acid will be attracted to the water. In this way, the soil is pulled free of the jersey and is suspended in the water. In a washing machine or with vigourous handwashing, this suspension can be rinsed off with clean water.



Definition: Soap

Soap is a surfactant that is used with water for washing and cleaning. Soap is made by reacting a fat with either sodium hydroxide (NaOH) or potassium hydroxide (KOH).

2. Detergents



Definition: Detergent

Detergents are compounds or mixtures of compounds that are used to assist cleaning. The term is often used to distinguish between soap and other chemical surfactants for cleaning.

Detergents are also cleaning products, but are composed of one or more surfactants. Depending on the type of cleaning that is needed, detergents may contain one or more of the following:

- Abrasives to scour a surface.
- Oxidants for bleaching and disinfection.
- *Enzymes* to digest proteins, fats or carbohydrates in stains. These are called *biological detergents*.

Exercise: The choralkali industry



- 1. The diagram above shows the sequence of steps that take place in the mercury cell.
 - (a) Name the 'raw material' in step 1.
 - (b) Give the chemical equation for the reaction that produces chlorine in step 2.
 - (c) What other product is formed in step 2.
 - (d) Name the reactants in step 4.
- 2. Approximately 30 million tonnes of chlorine are used throughout the world annually. Chlorine is produced industrially by the electrolysis of brine. The diagram represents a membrane cell used in the production of Cl_2 gas.



- (a) What ions are present in the electrolyte in the left hand compartment of the cell?
- (b) Give the equation for the reaction that takes place at the anode.
- (c) Give the equation for the reaction that takes place at the cathode.
- (d) What ion passes through the membrane while these reactions are taking place?

Chlorine is used to purify drinking water and swimming pool water. The substance responsible for this process is the weak acid, hypochlorous acid (HOCI).

- (e) One way of putting HOCl into a pool is to bubble chlorine gas through the water. Give an equation showing how bubbling $Cl_2(g)$ through water produces HOCl.
- (f) A common way of treating pool water is by adding 'granular chlorine'. Granular chlorine consists of the salt calcium hypochlorite, Ca(OCI)₂. Give an equation showing how this salt dissolves in water. Indicate the phase of each substance in the equation.
- (g) The OCl⁻ ion undergoes hydrolysis , as shown by the following equation: $OCl^- + H_2O \Leftrightarrow HOCl + OH^-$

Will the addition of granular chlorine to pure water make the water acidic, basic or will it remain neutral? Briefly explain your answer.

(IEB Paper 2, 2003)

23.4 The Fertiliser Industry

23.4.1 The value of nutrients

Nutrients are very important for life to exist. An **essential nutrient** is any chemical element that is needed for a plant to be able to grow from a seed and complete its life cycle. The same is true for animals. A *macronutrient* is one that is required in large quantities by the plant or animal, while a *micronutrient* is one that only needs to be present in small amounts for a plant or an animal to function properly.



Definition: Nutrient

A nutrient is a substance that is used in an organism's metabolism or physiology and which must be taken in from the environment.

In plants, the macronutrients include carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) and potassium (K). The source of each of these nutrients for plants, and their function, is summarised in table 23.1. Examples of micronutrients in plants include iron, chlorine, copper and zinc.

Nutrient	Source	Function
Carbon	Carbon dioxide in the	Component of organic
	air	molecules such as carbohy-
		drates, lipids and proteins
Hydrogen	Water from the soil	Component of organic
		molecules
Oxygen	Water from the soil	Component of organic
		molecules
Nitrogen	Nitrogen compounds	Part of plant proteins and
	in the soil	chlorophyll. Also boosts
		plant growth.
Phosphorus	Phosphates in the soil	Needed for photosynthesis,
		blooming and root growth
Potassium	Soil	Building proteins, part of
		chlorophyll and reduces dis-
		eases in plants

Table 23.1: The source and function of the macronutrients in plants

Animals need similar nutrients in order to survive. However since animals can't photosynthesise, they rely on plants to supply them with the nutrients they need. Think for example of the human diet. We can't make our own food and so we either need to eat vegetables, fruits and seeds (all of which are direct plant products) or the meat of other animals which would have fed on plants during their life. So most of the nutrients that animals need are obtained either directly or indirectly from plants. Table 23.2 summarises the functions of some of the macronutrients in animals.

Micronutrients also play an important function in animals. Iron for example, is found in haemoglobin, the blood pigment that is responsible for transporting oxygen to all the cells in the body.

Nutrients then, are essential for the survival of life. Importantly, obtaining nutrients starts with plants, which are able either to photosynthesise or to absorb the required nutrients from the soil. It is important therefore that plants are always able to access the nutrients that they need so that they will grow and provide food for other forms of life.

23.4.2 The Role of fertilisers

Plants are only able to absorb soil nutrients in a particular form. Nitrogen for example, is absorbed as **nitrates**, while phosphorus is absorbed as **phosphates**. The **nitrogen cycle** (chapter

Nutrient	Function	
Carbon	Component of organic compounds	
Hydrogen	Component of organic compounds	
Oxygen	Component of organic compounds	
Nitrogen	Component of nucleic acids and	
	proteins	
Phosphorus	Component of nucleic acids and	
	phospholipids	
Potassium	Helps in coordination and regulat-	
	ing the water balance in the body	

Table 23.2: The functions of animal macronutrients

19) describes the process that is involved in converting atmospheric nitrogen into a form that can be used by plants.

However, all these natural processes of maintaining soil nutrients take a long time. As populations grow and the demand for food increases, there is more and more strain on the land to produce food. Often, cultivation practices don't give the soil enough time to recover and to replace the nutrients that have been lost. Today, **fertilisers** play a very important role in restoring soil nutrients so that crop yields stay high. Some of these fertilisers are **organic** (e.g. compost, manure and fishmeal), which means that they started off as part of something living. Compost for example is often made up of things like vegetable peels and other organic remains that have been thrown away. Others are **inorganic** and can be made industrially. The advantage of these commercial fertilisers is that the nutrients are in a form that can be absorbed immediately by the plant.



Definition: Fertiliser

A fertiliser is a compound that is given to a plant to promote growth. Fertilisers usually provide the three major plant nutrients and most are applied via the soil so that the nutrients are absorbed by plants through their roots.

When you buy fertilisers from the shop, you will see three numbers on the back of the packet e.g. 18-24-6. These numbers are called the **NPK ratio**, and they give the percentage of nitrogen, phosphorus and potassium in that fertiliser. Depending on the types of plants you are growing, and the way in which you would like them to grow, you may need to use a fertiliser with a slightly different ratio. If you want to encourage root growth in your plant for example, you might choose a fertiliser with a greater amount of phosphorus. Look at the table below, which gives an idea of the amounts of nitrogen, phosphorus and potassium there are in different types of fertilisers. Fertilisers also provide other nutrients such as calcium, sulfur and magnesium.

Description	Grade (NPK %)
Ammonium nitrate	34-0-0
Urea	46-0-0
Bone Meal	4-21-1
Seaweed	1-1-5
Starter fertilisers	18-24-6
Equal NPK fertilisers	12-12-12
High N, low P and medium K fertilisers	25-5-15

Table 23.3: Common grades of some fertiliser materials

23.4.3 The Industrial Production of Fertilisers

The industrial production of fertilisers may involve several processes.

1. Nitrogen fertilisers

Making **nitrogen fertilisers** involves producing *ammonia*, which is then reacted with *oxy-gen* to produce *nitric acid*. Nitric acid is used to acidify phosphate rock to produce nitrogen fertilisers. The flow diagram below illustrates the processes that are involved. Each of these steps will be examined in more detail.



Figure 23.9: Flow diagram showing steps in the production of nitrogen fertilisers

(a) The Haber Process

The Haber process involves the reaction of nitrogen and hydrogen to produce ammonia. **Nitrogen** is produced through the **fractional distillation** of air. Fractional distillation is the separation of a mixture (remember that air is a mixture of different gases) into its component parts through various methods. **Hydrogen** can be produced through **steam reforming**. In this process, a hydrocarbon such as methane reacts with water to form carbon monoxide and hydrogen according to the following equation:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Nitrogen and hydrogen are then used in the Haber process. The equation for the Haber process is:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

(The reaction takes place in the presence of an iron (Fe) catalyst under conditions of 200 atmospheres (atm) and 450-500 degrees Celsius)



The Haber process developed in the early 20th century, before the start of World War 1. Before this, other sources of nitrogen for fertilisers had included saltpeter $(NaNO_3)$ from Chile and guano. Guano is the droppings of seabirds, bats and seals. By the 20th century, a number of methods had been developed to 'fix' atmospheric nitrogen. One of these was the Haber process, and it advanced through the work of two German men, Fritz Haber and Karl Bosch (The process is sometimes also referred to as the 'Haber-Bosch process'). They worked out what the best conditions were in order to get a high yield of ammonia, and found these to be high temperature and high pressure. They also experimented with different catalysts to see which worked best in that reaction. During World War 1, the ammonia that was produced through the Haber process was used to make explosives. One of the advantages for Germany was that, having perfected the Haber process, they did not need to rely on other countries for the chemicals that they needed to make them.

(b) The Ostwald Process

The Ostwald process is used to produce nitric acid from ammonia. Nitric acid can then be used in reactions that produce fertilisers. Ammonia is converted to nitric acid in two stages. First, it is oxidised by heating with oxygen in the presence of a platinum catalyst to form nitric oxide and water. This step is strongly exothermic, making it a useful heat source.

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

Stage two, which combines two reaction steps, is carried out in the presence of water. Initially nitric oxide is oxidised again to yield nitrogen dioxide:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

This gas is then absorbed by the water to produce nitric acid. Nitric oxide is also a product of this reaction. The nitric oxide (NO) is recycled, and the acid is concentrated to the required strength.

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

(c) The Nitrophosphate Process

The nitrophosphate process involves acidifying phosphate rock with nitric acid to produce a mixture of phosphoric acid and calcium nitrate:

$$Ca_3(PO_4)_2 + 6HNO_3 + 12H_2O \rightarrow 2H_3PO_4 + 3Ca(NO_3)_2 + 12H_2O$$

When calcium nitrate and phosphoric acid react with ammonia, a compound fertiliser is produced.

$$Ca(NO_3)_2 + 4H_3PO_4 + 8NH_3 \rightarrow CaHPO_4 + 2NH_4NO_3 + 8(NH_4)2HPO_4$$

If potassium chloride or potassium sulphate is added, the result will be NPK fertiliser.

(d) Other nitrogen fertilisers

 Urea ((NH₂)₂CO) is a nitrogen-containing chemical product which is produced on a large scale worldwide. Urea has the highest nitrogen content of all solid nitrogeneous fertilisers in common use (46.4%) and is produced by reacting ammonia with carbon dioxide.

Two reactions are involved in producing urea:

i.
$$2NH_3 + CO_2 \rightarrow H_2N - COONH_4$$

- ii. $H_2N COONH_4 \rightarrow (NH_2)_2CO + H_2O$
- Other common fertilisers are ammonium nitrate and ammonium sulphate. Ammonium nitrate is formed by reacting ammonia with nitric acid.

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

Ammonium sulphate is formed by reacting ammonia with sulphuric acid.

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

2. Phosphate fertilisers

The production of phosphate fertilisers also involves a number of processes. The first is the production of sulfuric acid through the **contact process**. Sulfuric acid is then used in a reaction that produces phosphoric acid. Phosphoric acid can then be reacted with phosphate rock to produce triple superphosphates.

(a) The production of sulfuric acid

Sulfuric acid is produced from sulfur, oxygen and water through the contact process. In the first step, sulfur is burned to produce sulfur dioxide.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

This is then oxidised to sulfur trioxide using oxygen in the presence of a vanadium(V) oxide catalyst.

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

$$453$$

Finally the sulfur trioxide is treated with water to produce 98-99% sulfuric acid.

 $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

(b) The production of phosphoric acid

The next step in the production of phosphate fertiliser is the reaction of sulfuric acid with phosphate rock to produce phosphoric acid (H_3PO_4). In this example, the phosphate rock is fluoropatite ($Ca_5F(PO_4)_3$).

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 5CaSO_42H_2O + HF + 3H_3PO_4$$

(c) The production of phosphates and superphosphates

When concentrated phosphoric acid reacts with ground phosphate rock, triple superphosphate is produced.

 $3Ca_3(PO_4)_2CaF_2 + 4H_3PO_4 + 9H_2O \rightarrow 9Ca(H_2PO_4)_2 + CaF_2$

3. Potassium

Potassium is obtained from **potash**, an impure form of potassium carbonate (K_2CO_3). Other potassium salts (e.g. KCI AND K_2O) are also sometimes included in fertilisers.

23.4.4 Fertilisers and the Environment: Eutrophication

Eutrophication is the enrichment of an ecosystem with chemical nutrients, normally by compounds that contain nitrogen or phosphorus. Eutrophication is considered a form of pollution because it promotes plant growth, favoring certain species over others. In aquatic environments, the rapid growth of certain types of plants can disrupt the normal functioning of an ecosystem, causing a variety of problems. Human society is impacted as well because eutrophication can decrease the resource value of rivers, lakes, and estuaries making recreational activities less enjoyable. Health-related problems can also occur if eutrophic conditions interfere with the treatment of drinking water.



Definition: Eutrophication

Eutrophication refers to an increase in chemical nutrients in an ecosystem. These chemical nutrients usually contain nitrogen or phosphorus.

In some cases, eutrophication can be a natural process that occurs very slowly over time. However, it can also be accelerated by certain human activities. Agricultural runoff, when excess fertilisers are washed off fields and into water, and sewage are two of the major causes of eutrophication. There are a number of impacts of eutrophication.

• A decrease in biodiversity (the number of plant and animal species in an ecosystem)

When a system is enriched with nitrogen, plant growth is rapid. When the number of plants increases in an aquatic system, they can block light from reaching deeper. Plants also consume oxygen for respiration, and if the oxygen content of the water decreases too much, this can cause other organisms such as fish to die.

• Toxicity

Sometimes, the plants that flourish during eutrophication can be toxic and may accumulate in the food chain.



South Africa's Department of Water Affairs and Forestry has a 'National Eutrophication Monitoring Programme' which was set up to monitor eutrophication in impoundments such as dams, where no monitoring was taking place.
Despite the impacts, there are a number of ways of preventing eutrophication from taking place. **Cleanup measures** can directly remove the excess nutrients such as nitrogen and phosphorus from the water. Creating **buffer zones** near farms, roads and rivers can also help. These act as filters and cause nutrients and sediments to be deposited there instead of in the aquatic system. **Laws** relating to the treatment and discharge of sewage can also help to control eutrophication. A final possible intervention is **nitrogen testing and modeling**. By assessing exactly how much fertiliser is needed by crops and other plants, farmers can make sure that they only apply just enough fertiliser. This means that there is no excess to run off into neighbouring streams during rain. There is also a cost benefit for the farmer.

Activity :: Discussion : Dealing with the consequences of eutrophication In many cases, the damage from eutrophication is already done. In groups, do the following:

- 1. List all the possible consequences of eutrophication that you can think of.
- 2. Suggest ways to solve these problems, that arise because of eutrophication.



Exercise: Chemical industry: Fertilisers

Why we need fertilisers

There is likely to be a gap between food production and demand in several parts of the world by 2020. Demand is influenced by population growth and urbanisation, as well as income levels and changes in dietary preferences.

The facts are as follows:

- There is an increasing world population to feed
- Most soils in the world used for large-scale, intensive production of crops lack the necessary nutrients for the crops

Conclusion: Fertilisers are needed!

The flow diagram below shows the main steps in the industrial preparation of two important solid fertilisers.



- 1. Write down the balanced chemical equation for the formation of the brown gas.
- 2. Write down the name of process Y.
- 3. Write down the chemical formula of liquid E.
- 4. Write down the chemical formulae of fertilisers C and D respectively. The following extract comes from an article on fertilisers:

A world without food for its people

A world with an environment poisoned through the actions of man Are two contributing factors towards a disaster scenario.

5. Write down THREE ways in which the use of fertilisers poisons the environment.

23.5 Electrochemistry and batteries

You will remember from chapter 17 that a **galvanic** cell (also known as a *voltaic* cell) is a type of electrochemical cell where a chemical reaction produces electrical energy. The **emf** of a galvanic cell is the difference in voltage between the two half cells that make it up. Galvanic cells have a number of applications, but one of the most important is their use in **batteries**. You will know from your own experience that we use batteries in a number of ways, including cars, torches, sound systems and cellphones to name just a few.

23.5.1 How batteries work

A battery is a device in which **chemical energy** is directly converted to **electrical energy**. It consists of one or more voltaic cells, each of which is made up of two half cells that are connected in series by a conductive electrolyte. The voltaic cells are connected in series in a battery. Each cell has a positive electrode (cathode), and a negative electrode (anode). These do not touch each other but are immersed in a solid or liquid electrolyte.

Each half cell has a net electromotive force (emf) or voltage. The voltage of the battery is the difference between the voltages of the half-cells. This potential difference between the two half cells is what causes an electric current to flow.

Batteries are usually divided into two broad classes:

- *Primary batteries* irreversibly transform chemical energy to electrical energy. Once the supply of reactants has been used up, the battery can't be used any more.
- Secondary batteries can be recharged, in other words, their chemical reactions can be reversed if electrical energy is supplied to the cell. Through this process, the cell returns to its original state. Secondary batteries can't be recharged forever because there is a gradual loss of the active materials and electrolyte. Internal corrosion can also take place.

23.5.2 Battery capacity and energy

The **capacity** of a battery, in other words its ability to produce an electric charge, depends on a number of factors. These include:

• Chemical reactions

The chemical reactions that take place in each of a battery's half cells will affect the voltage across the cell, and therefore also its capacity. For example, nickel-cadmium (NiCd) cells measure about 1.2V, and alkaline and carbon-zinc cells both measure about 1.5 volts. However, in other cells such as Lithium cells, the changes in electrochemical potential are much higher because of the reactions of lithium compounds, and so lithium cells can produce as much as 3 volts or more. The concentration of the chemicals that are involved will also affect a battery's capacity. The higher the concentration of the chemicals, the greater the capacity of the battery.

• Quantity of electrolyte and electrode material in cell

The greater the amount of electrolyte in the cell, the greater its capacity. In other words, even if the chemistry in two cells is the same, a larger cell will have a greater capacity than a small one. Also, the greater the surface area of the electrodes, the greater will be the capacity of the cell.

• Discharge conditions

A unit called an **Ampere hour** (Ah) is used to describe how long a battery will last. An ampere hour (more commonly known as an **amp hour**) is the amount of electric charge that is transferred by a current of one ampere for one hour. Battery manufacturers use a standard method to rate their batteries. So, for example, a 100 Ah battery will provide a current of 5 A for a period of 20 hours at room temperature. The capacity of the battery will depend on the rate at which it is discharged or used. If a 100 Ah battery is discharged at 50 A (instead of 5 A), the capacity will be *lower* than expected and the battery will run out *before* the expected 2 hours.

The relationship between the current, discharge time and capacity of a battery is expressed by **Peukert's law**:

$$C_p = I^k t$$

In the equation, C_p' represents the battery's capacity (Ah), I is the discharge current (A), k is the Peukert constant and t is the time of discharge (hours).

23.5.3 Lead-acid batteries

In a **lead-acid battery**, each cell consists of electrodes of lead (Pb) and lead (IV) oxide (PbO₂) in an electrolyte of sulfuric acid (H_2SO_4). When the battery discharges, both electrodes turn

into lead (II) sulphate (PbSO₄) and the electrolyte loses sulfuric acid to become mostly water.

The chemical half reactions that take place at the anode and cathode when the battery is **dis-charging** are as follows:

Anode (oxidation): $Pb(s) + SO_4^{2-}(aq) \Leftrightarrow PbSO_4(s) + 2e^-$ ($E^0 = -0.356$ V)

Cathode (reduction): $PbO_2(s) + SO_4^{2-}(aq) + 4H^+ + 2e^- \Leftrightarrow PbSO_4(s) + 2H_2O(l)$ (E⁰ = 1.685 V)

The overall reaction is as follows:

 $PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) + Pb(s) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

The emf of the cell is calculated as follows:

$$\begin{split} \mathsf{EMF} &= \mathsf{E} \text{ (cathode)- }\mathsf{E} \text{ (anode)} \\ \mathsf{EMF} &= +1.685 \text{ V} \text{ - (-0.356 V)} \\ \mathsf{EMF} &= +2.041 \text{ V} \end{split}$$

Since most batteries consist of six cells, the total voltage of the battery is approximately 12 V.

One of the important things about a lead-acid battery is that it can be **recharged**. The recharge reactions are the *reverse* of those when the battery is discharging.

The lead-acid battery is made up of a number of *plates* that maximise the surface area on which chemical reactions can take place. Each plate is a rectangular grid, with a series of holes in it. The holes are filled with a mixture of lead and sulfuric acid. This paste is pressed into the holes and the plates are then stacked together, with suitable separators between them. They are then placed in the battery container, after which acid is added (figure 23.10).



Figure 23.10: A lead-acid battery

Lead-acid batteries have a number of applications. They can supply high surge currents, are relatively cheap, have a long shelf life and can be recharged. They are ideal for use in cars,

where they provide the high current that is needed by the starter motor. They are also used in forklifts and as standby power sources in telecommunication facilities, generating stations and computer data centres. One of the disadvantages of this type of battery is that the battery's lead must be recycled so that the environment doesn't become contaminated. Also, sometimes when the battery is charging, hydrogen gas is generated at the cathode and this can cause a small explosion if the gas comes into contact with a spark.

23.5.4 The zinc-carbon dry cell

A simplified diagram of a zinc-carbon cell is shown in figure 23.11.



Figure 23.11: A zinc-carbon dry cell

A zinc-carbon cell is made up of an outer zinc container, which acts as the **anode**. The **cathode** is the central carbon rod, surrounded by a mixture of carbon and manganese (IV) oxide (MnO_2). The **electrolyte** is a paste of ammonium chloride (NH_4CI). A fibrous fabric separates the two electrodes, and a brass pin in the centre of the cell conducts electricity to the outside circuit.

The paste of ammonium chloride reacts according to the following half-reaction:

 $2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$

The manganese(IV) oxide in the cell removes the hydrogen produced above, according to the following reaction:

$$2MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$$

The combined result of these two reactions can be represented by the following half reaction, which takes place at the cathode:

Cathode: $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$

The anode half reaction is as follows:

Anode: $Zn(s) \rightarrow Zn^{2+} + 2e^{-}$

The overall equation for the cell is:

 $Zn(s) + 2MnO_2(s) + 2NH_4^+ \rightarrow Mn_2O_3(s) + H_2O + Zn(NH_3)_2^{2+}(aq)$ (E⁰ = 1.5 V)

Alkaline batteries are almost the same as zinc-carbon batteries, except that the electrolyte is potassium hydroxide (KOH), rather than ammonium chloride. The two half reactions in an alkaline battery are as follows:

Anode: $\operatorname{Zn}(s) + 2OH^{-}(aq) \rightarrow \operatorname{Zn}(OH)_{2}(s) + 2e^{-}$ Cathode: $2MnO_{2}(s) + H_{2}O(l) + 2e^{-} \rightarrow Mn_{2}O_{3}(s) + 2OH^{-}(aq)$

Zinc-carbon and alkaline batteries are cheap primary batteries and are therefore very useful in appliances such as remote controls, torches and radios where the power drain is not too high. The disadvantages are that these batteries can't be recycled and can leak. They also have a short shelf life. Alkaline batteries last longer than zinc-carbon batteries.



The idea behind today's common 'battery' was created by Georges Leclanche in France in the 1860's. The anode was a zinc and mercury alloyed rod, the cathode was a porous cup containing crushed MnO_2 . A carbon rod was inserted into this cup. The electrolyte was a liquid solution of ammonium chloride, and the cell was therefore called a *wet cell*. This was replaced by the *dry cell* in the 1880's. In the dry cell, the zinc can which contains the electrolyte, has become the anode, and the electrolyte is a paste rather than a liquid.

23.5.5 Environmental considerations

While batteries are very convenient to use, they can cause a lot of damage to the environment. They use lots of valuable resources as well as some potentially hazardous chemicals such as lead, mercury and cadmium. Attempts are now being made to recycle the different parts of batteries so that they are not disposed of in the environment, where they could get into water supplies, rivers and other ecosystems.

Exercise: Electrochemistry and batteries

A dry cell, as shown in the diagram below, does not contain a liquid electrolyte. The electrolyte in a typical zinc-carbon cell is a moist paste of ammonium chloride and zinc chloride.

(NOTE TO SELF: Insert diagram)

The paste of ammonium chloride reacts according to the following half-reaction:

 $2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$ (a)

Manganese(IV) oxide is included in the cell to remove the hydrogen produced during half-reaction (a), according to the following reaction:

$$2MnO_22(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$$
 (b)

The combined result of these two half-reactions can be represented by the following half reaction:

 $2NH_4^+(aq) + 2MnO_2(s) + 2e^- \rightarrow Mn_2O_3(s) + 2NH_3(g) + H_2O(l)$ (c)

1. Explain why it is important that the hydrogen produced in half-reaction (a) is removed by the manganese(IV) oxide.

In a zinc-carbon cell, such as the one above, half-reaction (c) and the half-reaction that takes place in the Zn/Zn^{2+} half-cell, produce an emf of 1,5 V under standard conditions.

- 2. Write down the half-reaction occurring at the anode.
- 3. Write down the net ionic equation occurring in the zinc-carbon cell.
- 4. Calculate the reduction potential for the cathode half-reaction.
- When in use the zinc casing of the dry cell becomes thinner, because it is oxidised. When not in use, it still corrodes. Give a reason for the latter observation.
- 6. Dry cells are generally discarded when 'flat'. Why is the carbon rod the most useful part of the cell, even when the cell is flat?

(DoE Exemplar Paper 2, 2007)

23.6 Summary

- The growth of South Africa's chemical industry was largely because of the mines, which needed explosives for their operations. One of South Africa's major chemical companies is Sasol. Other important chemical industries in the country are the chloralkali and fertiliser industries.
- All countries need energy resources such as oil and natural gas. Since South Africa doesn't
 have either of these resources, Sasol technology has developed to convert coal into liquid
 fuels.
- Sasol has three main operation focus areas: Firstly, the conversion of **coal to liquid fuel**, secondly the production and **refinement of crude oil** which has been imported, and thirdly the production of **liquid fuels from natural gas**.
- The conversion of coal to liquid fuels involves a Sasol/Lurgi gasification process, followed by the conversion of this synthesis gas into a range of hydrocarbons, using the Fischer-Tropsch technology in SAS reactors.
- Heavy hydrocarbons can be converted into light hydrcarbons through a process called cracking. Common forms of cracking are hydrocracking and steam cracking.
- With regard to crude oil, Sasol imports crude oil from Gabon and then refines this at the Natref refinery.
- Gas from Mozambique can be used to produce liquid fuels, through two processes: First, the gas must pass through an autothermal reactor to produce a synthesis gas. Secondly, this synthesis gas is passed through a **Sasol Slurry Phase Distillate** process to convert the gas to hydrocarbons.
- All industries have an impact on the **environment** through the consumption of natural resources such as water, and through the production of pollution gases such as carbon dioxide, hydrogen sulfides, nitrogen oxides and others.
- The **chloralkali industry** produces **chlorine** and **sodium hydroxide**. The main raw material is **brine** (NaCl).

- In industry, **electrolytic cells** are used to split the sodium chloride into its component ions to produce chlorine and sodium hydroxide. One of the challenges in this process is to keep the products of the electrolytic reaction (i.e. the chlorine and the sodium hydroxide) separate so that they don't react with each other. Specially designed electrolytic cells are needed to do this.
- There are three types of electrolytic cells that are used in this process: mercury cell, the diaphragm cell and the membrane cell.
- The mercury cell consists of two reaction vessels. The first reaction vessel contains a mercury cathode and a carbon anode. An electric current passed through the brine produces CI^- and Na^+ ions. The CI^- ions are oxidised to form chlorine gas at the anode. Na^+ ions combine with the mercury cathode to form a sodium-mercury amalgam. The sodium-mercury amalgam passes into the second reaction vessel containing water, where the Na^+ ions react with hydroxide ions from the water. Sodium hydroxide is the product of this reaction.
- One of the **environmental impacts** of using this type of cell, is the use of **mercury**, which is highly toxic.
- In the **diaphragm cell**, a porous diaphragm separates the anode and the cathode compartments. Chloride ions are oxidised to chlorine gas at the anode, while sodium ions produced at the cathode react with water to produce sodium hydroxide.
- The **membrane cell** is very similar to the diaphragm cell, except that the anode and cathode compartments are separated by an **ion-selective membrane** rather than by a diaphragm. Brine is only pumped into the anode compartment. Positive sodium ions pass through the membrane into the cathode compartment, which contains water. As with the other two cells, chlorine gas is produced at the anode and sodium hydroxide at the cathode.
- One use of sodium hydroxide is in the production of **soaps and detergents**, and so this is another important part of the chloralkali industry.
- To make soap, sodium hydroxide or potassium hydroxide react with a fat or an oil. In the reaction, the sodium or potassium ions replace the alcohol in the fat or oil. The product, a **sodium or potassium salt of a fatty acid**, is what soap is made of.
- The fatty acids in soap have a **hydrophilic** and a **hydrophobic** part in each molecule, and this helps to loosen dirt and clean items.
- **Detergents** are also cleaning products, but are made up of a mixture of compounds. They may also have other components added to them to give certain characteristics. Some of these additives may be abrasives, oxidants or enzymes.
- The fertiliser industry is another important chemical industry.
- All plants need certain **macronutrients** (e.g. carbon, hydrogen, oxygen, potassium, nitrogen and phosphorus) and **micronutrients** (e.g. iron, chlorine, copper and zinc) in order to survive. Fertilisers provide these nutrients.
- In plants, most nutrients are obtained from the atmosphere or from the soil.
- Animals also need similar nutrients, but they obtain most of these directly from plants or plant products. They may also obtain them from other animals, which may have fed on plants during their life.
- The fertiliser industry is very important in ensuring that plants and crops receive the correct nutrients in the correct quantities to ensure maximum growth.
- Nitrogen fertilisers can be produced industrially using a number of chemical processes: The Haber process reacts nitrogen and hydrogen to produce ammonia; the Ostwald process reacts oxygen and ammonia to produce nitric acid; the nitrophosphate process reacts nitric acid with phosphate rock to produce compound fertilisers.

- Phosphate fertilisers are also produced through a series of reactions. The contact process produces sulfuric acid. Sulfuric acid then reacts with phosphate rock to produce phosphoric acid, after which phosphoric acid reacts with ground phosphate rock to produce fertilisers such as triple superphosphate.
- Potassium is obtained from **potash**.
- Fertilisers can have a damaging effect on the environment when they are present in high quantities in ecosystems. They can lead to **eutrophication**. A number of preventative actions can be taken to reduce these impacts.
- Another important part of the chemical industry is the production of **batteries**.
- A battery is a device that changes chemical energy into electrical energy.
- A battery consists of one or more **voltaic cells**, each of which is made up of two half cells that are connected in series by a conductive electrolyte. Each half cell has a net electromotive force (emf) or voltage. The net voltage of the battery is the difference between the voltages of the half-cells. This potential difference between the two half cells is what causes an electric current to flow.
- A primary battery cannot be recharged, but a secondary battery can be recharged.
- The capacity of a battery depends on the chemical reactions in the cells, the quantity of electrolyte and electrode material in the cell, and the discharge conditions of the battery.
- The relationship between the current, discharge time and capacity of a battery is expressed by Peukert's law:

$$C_p = I^k t$$

In the equation, C_p' represents the battery's capacity (Ah), I is the discharge current (A), k is the Peukert constant and t is the time of discharge (hours).

- Two common types of batteries are lead-acid batteries and the zinc-carbon dry cell.
- In a **lead-acid battery**, each cell consists of electrodes of lead (Pb) and lead (IV) oxide (PbO₂) in an electrolyte of sulfuric acid (H_2SO_4). When the battery discharges, both electrodes turn into lead (II) sulphate (PbSO₄) and the electrolyte loses sulfuric acid to become mostly water.
- A zinc-carbon cell is made up of an outer zinc container, which acts as the anode. The cathode is the central carbon rod, surrounded by a mixture of carbon and manganese (IV) oxide (MnO₂). The electrolyte is a paste of ammonium chloride (NH₄Cl). A fibrous fabric separates the two electrodes, and a brass pin in the centre of the cell conducts electricity to the outside circuit.
- Despite their many advantages, batteries are made of potentially toxic materials and can be damaging to the **environment**.



Exercise: Summary Exercise

- 1. Give one word or term for each of the following descriptions:
 - (a) A solid organic compound that can be used to produce liquid fuels.
 - (b) The process used to convert heavy hydrocarbons into light hydrocarbons.
 - (c) The process of separating nitrogen from liquid air.
 - (d) The main raw material in the chloralkali industry.
 - (e) A compound given to a plant to promote growth.

- (f) An electrolyte used in lead-acid batteries.
- Indicate whether each of the following statements is true or false. If the statement is false, rewrite the statement correctly.
 - (a) The longer the hydrocarbon chain in an organic compound, the more likely it is to be a solid at room temperature.
 - (b) The main elements used in fertilisers are nitrogen, phosphorus and potassium.
 - (c) A soap molecule is composed of an alcohol molecule and three fatty acids.
 - (d) During the industrial preparation of chlorine and sodium hydroxide, chemical energy is converted to electrical energy.
- 3. For each of the following questions, choose the one correct answer from the list provided.
 - (a) The sequence of processes that best describes the conversion of coal to liquid fuel is:
 - i. coal \rightarrow gas purification \rightarrow SAS reactor \rightarrow liquid hydrocarbon
 - ii. coal \rightarrow autothermal reactor \rightarrow Sasol slurry phase F-T reactor \rightarrow liquid hydrocarbon
 - iii. coal \rightarrow coal purification \rightarrow synthesis gas \rightarrow oil
 - iv. coal \rightarrow coal gasification \rightarrow gas purification \rightarrow SAS reactor \rightarrow liquid hydrocarbons
 - (b) The half-reaction that takes place at the cathode of a mercury cell in the chloralkali industry is:
 - i. $2Cl^- \rightarrow Cl_2 + 2e^-$
 - ii. $2Na^+ + 2e^- \rightarrow 2Na$
 - iii. $2H^+ + 2e^- \rightarrow H_2$
 - iv. $NaCl + H_2O \rightarrow NaOH + HCl$
 - (c) In a zinc-carbon dry cell...
 - i. the electrolyte is manganese (IV) oxide
 - ii. zinc is oxidised to produce electrons
 - iii. zinc is reduced to produce electrons
 - iv. manganese (IV) dioxide acts as a reducing agent

4. Chloralkali manufacturing process

The chloralkali (also called 'chlorine-caustic') industry is one of the largest electrochemical technologies in the world. Chlorine is produced using three types of electrolytic cells. The simplified diagram below shows a membrane cell.



- (a) Give two reasons why the membrane cell is the preferred cell for the preparation of chlorine.
- (b) Why do you think it is advisable to use inert electrodes in this process?
- (c) Write down the equation for the half-reaction taking place at electrode M.
- (d) Which gas is chlorine gas? Write down only Gas A or Gas B.

(e) Briefly explain how sodium hydroxide forms in this cell.

(DoE Exemplar Paper 2,2007)

5. The production of nitric acid is very important in the manufacture of fertilisers. Look at the diagram below, which shows part of the fertiliser production process, and then answer the questions that follow.



- (a) Name the process at (1).
- (b) Name the gas at (2).

-

- (c) Name the process at (3) that produces gas (2).
- (d) Name the product at (4).
- (e) Name two fertilisers that can be produced from nitric acid.
- 6. A lead-acid battery has a number of different components. Match the description in Column A with the correct word or phrase in Column B. All the descriptions in Column A relate to lead-acid batteries.

Column A	Column B
The electrode metal	Lead sulphate
Electrolyte	Mercury
A product of the overall cell reaction	Electrolytic
An oxidising agent in the cathode half-reaction	Lead
Type of cells in a lead-acid battery	Sulfuric acid
	Ammonium chloride
	Lead oxide
	Galvanic

Appendix A

GNU Free Documentation License

Version 1.2, November 2002 Copyright © 2000,2001,2002 Free Software Foundation, Inc. 59 Temple Place, Suite 330, Boston, MA 02111-1307 USA Everyone is permitted to copy and distribute verbatim copies of this license document, but changing it is not allowed.

PREAMBLE

The purpose of this License is to make a manual, textbook, or other functional and useful document "free" in the sense of freedom: to assure everyone the effective freedom to copy and redistribute it, with or without modifying it, either commercially or non-commercially. Secondarily, this License preserves for the author and publisher a way to get credit for their work, while not being considered responsible for modifications made by others.

This License is a kind of "copyleft", which means that derivative works of the document must themselves be free in the same sense. It complements the GNU General Public License, which is a copyleft license designed for free software.

We have designed this License in order to use it for manuals for free software, because free software needs free documentation: a free program should come with manuals providing the same freedoms that the software does. But this License is not limited to software manuals; it can be used for any textual work, regardless of subject matter or whether it is published as a printed book. We recommend this License principally for works whose purpose is instruction or reference.

APPLICABILITY AND DEFINITIONS

This License applies to any manual or other work, in any medium, that contains a notice placed by the copyright holder saying it can be distributed under the terms of this License. Such a notice grants a world-wide, royalty-free license, unlimited in duration, to use that work under the conditions stated herein. The "Document", below, refers to any such manual or work. Any member of the public is a licensee, and is addressed as "you". You accept the license if you copy, modify or distribute the work in a way requiring permission under copyright law.

A "Modified Version" of the Document means any work containing the Document or a portion of it, either copied verbatim, or with modifications and/or translated into another language.

A "Secondary Section" is a named appendix or a front-matter section of the Document that deals exclusively with the relationship of the publishers or authors of the Document to the Document's overall subject (or to related matters) and contains nothing that could fall directly within that overall subject. (Thus, if the Document is in part a textbook of mathematics, a Secondary Section may not explain any mathematics.) The relationship could be a matter of historical connection with the subject or with related matters, or of legal, commercial, philosophical, ethical or political position regarding them.

The "Invariant Sections" are certain Secondary Sections whose titles are designated, as being those of Invariant Sections, in the notice that says that the Document is released under this License. If a section does not fit the above definition of Secondary then it is not allowed to be designated as Invariant. The Document may contain zero Invariant Sections. If the Document does not identify any Invariant Sections then there are none.

The "Cover Texts" are certain short passages of text that are listed, as Front-Cover Texts or Back-Cover Texts, in the notice that says that the Document is released under this License. A Front-Cover Text may be at most 5 words, and a Back-Cover Text may be at most 25 words.

A "Transparent" copy of the Document means a machine-readable copy, represented in a format whose specification is available to the general public, that is suitable for revising the document straightforwardly with generic text editors or (for images composed of pixels) generic paint programs or (for drawings) some widely available drawing editor, and that is suitable for input to text formatters or for automatic translation to a variety of formats suitable for input to text formatters. A copy made in an otherwise Transparent file format whose markup, or absence of markup, has been arranged to thwart or discourage subsequent modification by readers is not Transparent. An image format is not Transparent if used for any substantial amount of text. A copy that is not "Transparent" is called "Opaque".

Examples of suitable formats for Transparent copies include plain ASCII without markup, Texinfo input format, LATEX input format, SGML or XML using a publicly available DTD and standard-conforming simple HTML, PostScript or PDF designed for human modification. Examples of transparent image formats include PNG, XCF and JPG. Opaque formats include proprietary formats that can be read and edited only by proprietary word processors, SGML or XML for which the DTD and/or processing tools are not generally available, and the machine-generated HTML, PostScript or PDF produced by some word processors for output purposes only.

The "Title Page" means, for a printed book, the title page itself, plus such following pages as are needed to hold, legibly, the material this License requires to appear in the title page. For works in formats which do not have any title page as such, "Title Page" means the text near the most prominent appearance of the work's title, preceding the beginning of the body of the text.

A section "Entitled XYZ" means a named subunit of the Document whose title either is precisely XYZ or contains XYZ in parentheses following text that translates XYZ in another language. (Here XYZ stands for a specific section name mentioned below, such as "Acknowledgements", "Dedications", "Endorsements", or "History".) To "Preserve the Title" of such a section when you modify the Document means that it remains a section "Entitled XYZ" according to this definition.

The Document may include Warranty Disclaimers next to the notice which states that this License applies to the Document. These Warranty Disclaimers are considered to be included by reference in this License, but only as regards disclaiming warranties: any other implication that these Warranty Disclaimers may have is void and has no effect on the meaning of this License.

VERBATIM COPYING

You may copy and distribute the Document in any medium, either commercially or non-commercially, provided that this License, the copyright notices, and the license notice saying this License applies to the Document are reproduced in all copies, and that you add no other conditions whatsoever to those of this License. You may not use technical measures to obstruct or control the reading or further copying of the copies you make or distribute. However, you may accept compensation in exchange for copies. If you distribute a large enough number of copies you must also follow the conditions in section A.

You may also lend copies, under the same conditions stated above, and you may publicly display copies.

COPYING IN QUANTITY

If you publish printed copies (or copies in media that commonly have printed covers) of the Document, numbering more than 100, and the Document's license notice requires Cover Texts,

you must enclose the copies in covers that carry, clearly and legibly, all these Cover Texts: Front-Cover Texts on the front cover, and Back-Cover Texts on the back cover. Both covers must also clearly and legibly identify you as the publisher of these copies. The front cover must present the full title with all words of the title equally prominent and visible. You may add other material on the covers in addition. Copying with changes limited to the covers, as long as they preserve the title of the Document and satisfy these conditions, can be treated as verbatim copying in other respects.

If the required texts for either cover are too voluminous to fit legibly, you should put the first ones listed (as many as fit reasonably) on the actual cover, and continue the rest onto adjacent pages.

If you publish or distribute Opaque copies of the Document numbering more than 100, you must either include a machine-readable Transparent copy along with each Opaque copy, or state in or with each Opaque copy a computer-network location from which the general network-using public has access to download using public-standard network protocols a complete Transparent copy of the Document, free of added material. If you use the latter option, you must take reasonably prudent steps, when you begin distribution of Opaque copies in quantity, to ensure that this Transparent copy will remain thus accessible at the stated location until at least one year after the last time you distribute an Opaque copy (directly or through your agents or retailers) of that edition to the public.

It is requested, but not required, that you contact the authors of the Document well before redistributing any large number of copies, to give them a chance to provide you with an updated version of the Document.

MODIFICATIONS

You may copy and distribute a Modified Version of the Document under the conditions of sections A and A above, provided that you release the Modified Version under precisely this License, with the Modified Version filling the role of the Document, thus licensing distribution and modification of the Modified Version to whoever possesses a copy of it. In addition, you must do these things in the Modified Version:

- 1. Use in the Title Page (and on the covers, if any) a title distinct from that of the Document, and from those of previous versions (which should, if there were any, be listed in the History section of the Document). You may use the same title as a previous version if the original publisher of that version gives permission.
- 2. List on the Title Page, as authors, one or more persons or entities responsible for authorship of the modifications in the Modified Version, together with at least five of the principal authors of the Document (all of its principal authors, if it has fewer than five), unless they release you from this requirement.
- 3. State on the Title page the name of the publisher of the Modified Version, as the publisher.
- 4. Preserve all the copyright notices of the Document.
- 5. Add an appropriate copyright notice for your modifications adjacent to the other copyright notices.
- Include, immediately after the copyright notices, a license notice giving the public permission to use the Modified Version under the terms of this License, in the form shown in the Addendum below.
- 7. Preserve in that license notice the full lists of Invariant Sections and required Cover Texts given in the Document's license notice.
- 8. Include an unaltered copy of this License.
- 9. Preserve the section Entitled "History", Preserve its Title, and add to it an item stating at least the title, year, new authors, and publisher of the Modified Version as given on the Title Page. If there is no section Entitled "History" in the Document, create one stating the title, year, authors, and publisher of the Document as given on its Title Page, then add an item describing the Modified Version as stated in the previous sentence.

- 10. Preserve the network location, if any, given in the Document for public access to a Transparent copy of the Document, and likewise the network locations given in the Document for previous versions it was based on. These may be placed in the "History" section. You may omit a network location for a work that was published at least four years before the Document itself, or if the original publisher of the version it refers to gives permission.
- 11. For any section Entitled "Acknowledgements" or "Dedications", Preserve the Title of the section, and preserve in the section all the substance and tone of each of the contributor acknowledgements and/or dedications given therein.
- 12. Preserve all the Invariant Sections of the Document, unaltered in their text and in their titles. Section numbers or the equivalent are not considered part of the section titles.
- 13. Delete any section Entitled "Endorsements". Such a section may not be included in the Modified Version.
- 14. Do not re-title any existing section to be Entitled "Endorsements" or to conflict in title with any Invariant Section.
- 15. Preserve any Warranty Disclaimers.

If the Modified Version includes new front-matter sections or appendices that qualify as Secondary Sections and contain no material copied from the Document, you may at your option designate some or all of these sections as invariant. To do this, add their titles to the list of Invariant Sections in the Modified Version's license notice. These titles must be distinct from any other section titles.

You may add a section Entitled "Endorsements", provided it contains nothing but endorsements of your Modified Version by various parties-for example, statements of peer review or that the text has been approved by an organisation as the authoritative definition of a standard.

You may add a passage of up to five words as a Front-Cover Text, and a passage of up to 25 words as a Back-Cover Text, to the end of the list of Cover Texts in the Modified Version. Only one passage of Front-Cover Text and one of Back-Cover Text may be added by (or through arrangements made by) any one entity. If the Document already includes a cover text for the same cover, previously added by you or by arrangement made by the same entity you are acting on behalf of, you may not add another; but you may replace the old one, on explicit permission from the previous publisher that added the old one.

The author(s) and publisher(s) of the Document do not by this License give permission to use their names for publicity for or to assert or imply endorsement of any Modified Version.

COMBINING DOCUMENTS

You may combine the Document with other documents released under this License, under the terms defined in section A above for modified versions, provided that you include in the combination all of the Invariant Sections of all of the original documents, unmodified, and list them all as Invariant Sections of your combined work in its license notice, and that you preserve all their Warranty Disclaimers.

The combined work need only contain one copy of this License, and multiple identical Invariant Sections may be replaced with a single copy. If there are multiple Invariant Sections with the same name but different contents, make the title of each such section unique by adding at the end of it, in parentheses, the name of the original author or publisher of that section if known, or else a unique number. Make the same adjustment to the section titles in the list of Invariant Sections in the license notice of the combined work.

In the combination, you must combine any sections Entitled "History" in the various original documents, forming one section Entitled "History"; likewise combine any sections Entitled "Ac-knowledgements", and any sections Entitled "Dedications". You must delete all sections Entitled "Endorsements".

COLLECTIONS OF DOCUMENTS

You may make a collection consisting of the Document and other documents released under this License, and replace the individual copies of this License in the various documents with a single copy that is included in the collection, provided that you follow the rules of this License for verbatim copying of each of the documents in all other respects.

You may extract a single document from such a collection, and distribute it individually under this License, provided you insert a copy of this License into the extracted document, and follow this License in all other respects regarding verbatim copying of that document.

AGGREGATION WITH INDEPENDENT WORKS

A compilation of the Document or its derivatives with other separate and independent documents or works, in or on a volume of a storage or distribution medium, is called an "aggregate" if the copyright resulting from the compilation is not used to limit the legal rights of the compilation's users beyond what the individual works permit. When the Document is included an aggregate, this License does not apply to the other works in the aggregate which are not themselves derivative works of the Document.

If the Cover Text requirement of section A is applicable to these copies of the Document, then if the Document is less than one half of the entire aggregate, the Document's Cover Texts may be placed on covers that bracket the Document within the aggregate, or the electronic equivalent of covers if the Document is in electronic form. Otherwise they must appear on printed covers that bracket the whole aggregate.

TRANSLATION

Translation is considered a kind of modification, so you may distribute translations of the Document under the terms of section A. Replacing Invariant Sections with translations requires special permission from their copyright holders, but you may include translations of some or all Invariant Sections in addition to the original versions of these Invariant Sections. You may include a translation of this License, and all the license notices in the Document, and any Warranty Disclaimers, provided that you also include the original English version of this License and the original versions of those notices and disclaimers. In case of a disagreement between the translation and the original version of this License or a notice or disclaimer, the original version will prevail.

If a section in the Document is Entitled "Acknowledgements", "Dedications", or "History", the requirement (section A) to Preserve its Title (section A) will typically require changing the actual title.

TERMINATION

You may not copy, modify, sub-license, or distribute the Document except as expressly provided for under this License. Any other attempt to copy, modify, sub-license or distribute the Document is void, and will automatically terminate your rights under this License. However, parties who have received copies, or rights, from you under this License will not have their licenses terminated so long as such parties remain in full compliance.

FUTURE REVISIONS OF THIS LICENSE

The Free Software Foundation may publish new, revised versions of the GNU Free Documentation License from time to time. Such new versions will be similar in spirit to the present version, but may differ in detail to address new problems or concerns. See http://www.gnu.org/copyleft/.

Each version of the License is given a distinguishing version number. If the Document specifies that a particular numbered version of this License "or any later version" applies to it, you have the option of following the terms and conditions either of that specified version or of any later version that has been published (not as a draft) by the Free Software Foundation. If the Document does not specify a version number of this License, you may choose any version ever published (not as a draft) by the Free Software Foundation.

ADDENDUM: How to use this License for your documents

To use this License in a document you have written, include a copy of the License in the document and put the following copyright and license notices just after the title page:

Copyright © YEAR YOUR NAME. Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.2 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled "GNU Free Documentation License".

If you have Invariant Sections, Front-Cover Texts and Back-Cover Texts, replace the "with...Texts." line with this:

with the Invariant Sections being LIST THEIR TITLES, with the Front-Cover Texts being LIST, and with the Back-Cover Texts being LIST.

If you have Invariant Sections without Cover Texts, or some other combination of the three, merge those two alternatives to suit the situation.

If your document contains nontrivial examples of program code, we recommend releasing these examples in parallel under your choice of free software license, such as the GNU General Public License, to permit their use in free software.