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STUDY GUIDE:

CHEMISTRY HL

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IB Academy Chemistry Study Guide

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Welcome to the IB.Academy Study Guide for IB Chemistry High Level.

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For this Chemistry HL guide, we incorporated everything you need to know for your final exam. The guide is broken down into manageable chapters based on the syllabus topics. The chapter is then further divided into subtopics.

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QUANTITATIVE CHEMISTRY

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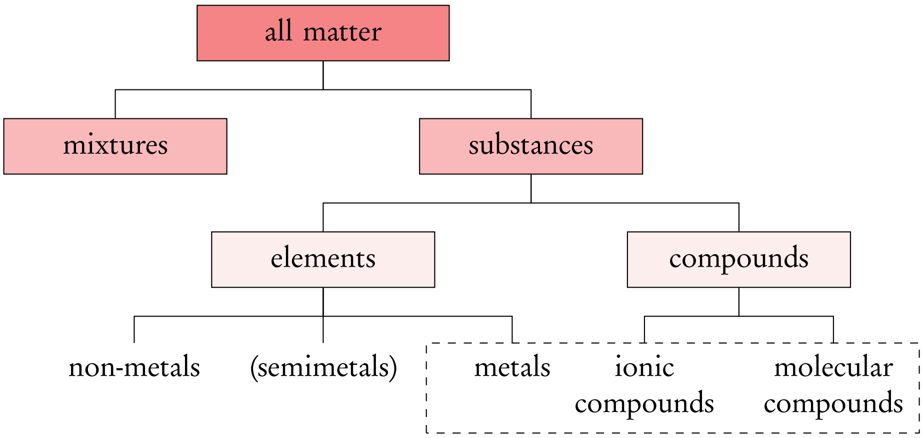
1.1 Types and states of matter



Classification of matter

Substance has a definite chemical composition and characteristic properties

Mixture contains multiple substances that retain their individual properties because they are not chemically bonded, which can be separated using the difference between the individual properties of each substance.

Homogeneous mixture:
Components are in the same phase, particles are distributed equally over the mixture
e.g. solution, alloy

Heterogeneous mixture:
Components are not all in the same phase, there are physical boundaries between the components.
e.g. suspension, emulsion

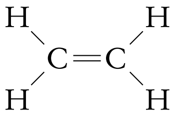
Classification of matter:	type of element(s):
metal	metal
ionic compound	metal + non-metal
molecular compound	non-metal

Elements are atoms that have the same number of protons. Elemental substances contain one type of element (e.g., Na, Fe, H_2, Cl_2, S_8, …)

Compounds at least *two different elements* combine to form a compound

The chemical composition of a substance is expressed in a chemical formula, which shows the number of each atom in a substance (e.g. H_2O), or the ratio of ions in an ionic compound (e.g. $MgCl_2$).

Note that for ionic compounds only the empirical formula is used, because ions assemble in a whole number ratio in a lattice, but not as molecules.

	molecular formula	structural formula	empirical formula
example	C_2H_4		CH_2
showing	number of atoms	bonding between the atoms	simplest number ratio of atoms

Example.

Which compound has the empirical formula with the greatest mass?

	molecular formula	divisible by	empirical formula	
A.	C_2H_6	2	CH_3	
B.	C_4H_{10}	2	C_2H_5	← greatest mass
C.	C_5H_{10}	5	CH_2	
D.	C_6H_6	6	CH	

Find the empirical formula given weight percentage composition

A compound is found to contain 64.80 % C, 13.62 % H, and 21.58 % O_2 by weight. What is the empirical formula for this compound?

1. Tabulate and assume 100 g

	C	H	O
grams	64.80 g	13.62 g	21.58 g

2. Convert the masses to moles (divide by the atomic mass)

	C	H	O
grams	64.80 g	13.62 g	21.58 g
moles	5.396 mol	13.49 mol	1.344 mol

3. Divide by the lowest, seeking the smallest whole-number ratio

	C	H	O
grams	64.80 g	13.62 g	21.58 g
moles	5.396 mol	13.49 mol	1.344 mol
simplest ratio	4	10	1

4. Write the empirical formula $C_4H_{10}O$

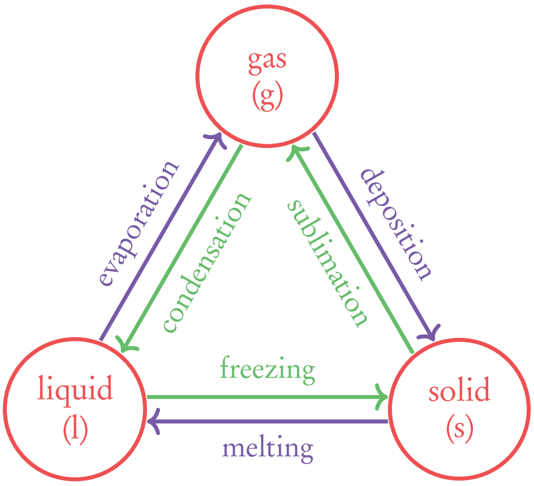
Derive the molecular formula from the empirical formula

From the previous, derive the molecular formula if the molecular mass is $222.4\,\mathrm{g\,mol^{-1}}$.

1.	$\dfrac{\text{molecular mass}}{\text{mass of the empirical formula}}$	$\dfrac{222.4\,\mathrm{g\,mol^{-1}}}{4\cdot 12.01+10\cdot 1.01+16.00\,\mathrm{g\,mol^{-1}}}=3$
2.	write the molecular formula	$C_{12}H_{30}O_3$ (since the molecule is 3 times the mass of the empirical formula)

To determine the molecular formula instead of the empirical formula, the molecular mass must also be given.

Phase changes and states of matter



The *state* of a substance is indicated as (s), (l) or (g).
Additionally, when a substance is dissolved in water we can indicate the phase as (aq).

	solid (s)	liquid (l)	gas (g)
movement of particles	vibrational	free movement	free movement
distance between particles	close	close	far apart
fixed volume	yes	yes	no, compressable
fixed shape	yes, rigid	no	no

1.2 Chemical reactions

Chemical reaction a process that leads to the transformation of one set of chemical substances to another, thus changing their chemical formulae

Combustion reaction a chemical reaction between a fuel and O_2; which compounds form depends on which elements the fuel contains

fuel contains	combustion product	effect (environmental)
C	CO_2 (complete)	greenhouse gas
	CO (incomplete)	toxic to animals
H	H_2O	—
S	SO_2	acid rain (see chapter 8)
N	NO_x	acid rain (see chapter 8)

Balancing and stoichiometry

To balance reactions we use the conservation of mass, which states that the number of atoms before and after a reaction must be equal, and the conservation of charge, which states that the charge before and after a reaction must also be equal.

Stoichiometric coefficients the numbers placed in front of substances in order to balance chemical reactions

Stoichiometry the quantitative relationships between substances in a chemical reaction (molar ratios)

Example.

Balance the reaction: $\ldots C_{10}H_{22} + \ldots O_2 \longrightarrow \ldots H_2O + \ldots CO_2$

The trick to balancing chemical reactions is to *balance elements in order of occurance*.

Check which elements occur in the least number of substances. Both C and H occur in one substance before and after the reaction arrow, so balance these first:

$1\, C_{10}H_{22} + O_2 \longrightarrow 11\, H_2O + 10\, CO_2$

O occurs in one substance before the reaction equation and in two substances after the reaction arrow, so balance O next. On the right there are 31 O-atoms, so on the left we need $\frac{31}{2}$ O_2 molecules.

$1\, C_{10}H_{22} + \frac{31}{2}\, O_2 \longrightarrow 11\, H_2O + 10\, CO_2$ (multiply by 2 to get rid of the fraction:)

$2\, C_{10}H_{22} + 31\, O_2 \longrightarrow 22\, H_2O + 20\, CO_2$

The balanced reaction equation shows the quantitative relationship (or stoichiometry) between reactants and products. In the example above: 2 $C_{10}H_{22}$ molecules react with 31 O_2 molecules, forming 22 H_2O molecules and 20 CO_2 molecules.

1.3 Mole concept and chemical calculations

Mole (n) the amount of substance which contains $N_A = 6.02 \times 10^{23}$ particles (atoms, molecules, ions, electrons, or other physical particles)

Avogadro's constant (N_A) 6.02×10^{23} particles/mol

When buying eggs, you can request one dozen eggs from old-lady Mme. Oeuf. It is a convenient expression, since the packaging contains 12 eggs. So a dozen is an alternative way to express "12".

The mole is analogously an alternative way to express the number of entities (6.02×10^{23}). This number is convenient to represent chemical amounts.

A dozen is a grouping of 12, so: 2 dozen is a grouping of 24.	A mole is a grouping of 6.0×10^{23}, so: 2 mole is a grouping of 1.2×10^{24}.

The mole concept is a necessity in chemical calculations. Since we constantly deal with *huge* numbers of particles in chemistry, expressing the number of particles in moles is more convenient. But more importantly, particles react and form in a particular stoichiometric ratio (molar ratio) in chemical reactions.

Take $2H_2 + O_2 \longrightarrow 2H_2O$; two molecules of H_2 will react with one molecule of O_2.

This *does not* mean that two grams of H_2 will react with one gram of O_2, since the masses of H_2 and O_2 molecules are not equal. This *does* mean that two moles of H_2 will react with one mole of O_2, but also that 1.8×10^{-3} mol H_2 will react with 0.9×10^{-3} mol O_2. Furthermore, in chemistry we constantly use huge ensembles of molecules. Using moles allows us to use much simpler numbers.

Relative and average mass

The relative masses are all measured relative to the atomic mass unit (u): defined as $^1/_{12}$ of the atomic mass of a ^{12}C atom. And they are all average: the weighed arithmatic mean of all isotopes and their terrestial natural abundancies.

Relative atomic mass (A_r) the weighed mean of all the isotopes of one element and their natural abundances, relative to one atomic mass unit, which is $^1/_{12}$ of the mass of a ^{12}C atom

Relative molecular mass (M_r) is the sum of the relative atomic masses of all the atoms in the molecular formula

Relative formula mass (M_r) applies to ionic compounds, and it is similar to the relative molecular mass and also calculated in the same way.

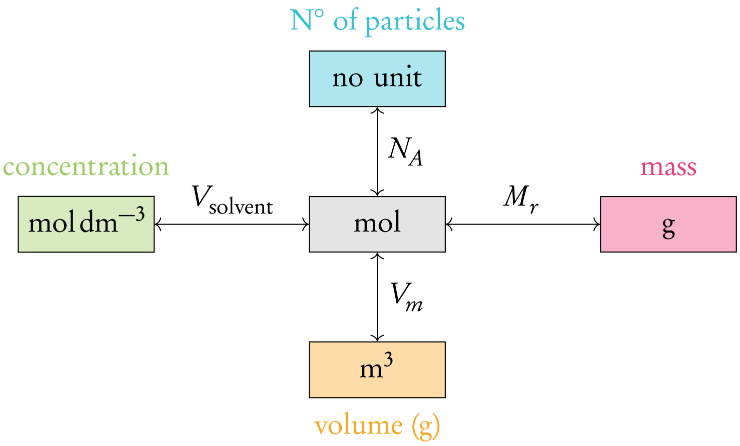
Molar mass M the mass of a substance *per one mole* expressed in $\mathrm{g\,mol^{-1}}$

Molecules have a well-defined number of atoms, but ionic compounds do not consist of a particular number of ions, rather of ions in a particular ratio.

1.3.1 Unit conversion

Roadmap to chemical calculations

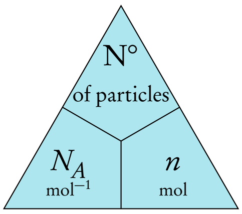
It is much easier to measure some physical quantity of a sample, such as its mass, than it is to count the number of particles in the sample. Therefore, you will have to convert various quantities to mole and back. The figure below gives an overview of the quantities that can be converted to moles and back, and what other quantity you will need to do so.



Mole ⟷ number of particles

The number of particles can be expressed in the amount of moles, or in the number of particles. Because $1\,\text{mol} = 6.02 \times 10^{23}$ particles. The quantities express the same thing, but use different values in doing so. It's like saying "a dozen eggs" to express 12 eggs.

The relationship between the number of particles and the amount in mol is given by:



$$\text{N° of particles} = n \cdot N_A$$

N° of particles = amount [no units]
n = chemical amount [mol]
N_A = Avogadro's constant $6.02 \times 10^{23}\,\text{mol}^{-1}$

Example.

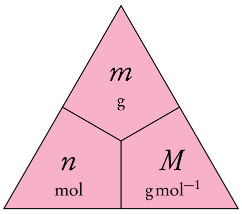
How many N-atoms are there in 1.0×10^{-2} mol NH_3NO_3?
N° of particles $= n \cdot N_A = 1.0 \times 10^{-2}\,\text{mol} \cdot 6.02 \times 10^{23}\,\text{mol}^{-1} = 6.02 \times 10^{21}$ molecules,
per molecule there are 2 N-atoms (mole ratio molecules : N-atoms = 1 : 2),
so $2 \cdot 6.02 \times 10^{21} = 1.2 \times 10^{22}$ N-atoms.

What is the total number of atoms in 0.20 mol of propanone, CH_3COCH_3?
N° of particles $= n \cdot N_A = 0.20\,\text{mol} \cdot 6.02 \times 10^{23}\,\text{mol}^{-1} = 1.2 \times 10^{23}$ molecules,
per molecule there are 10 atoms (mole ratio molecules : atoms = 1 : 10),
so $10 \cdot 1.2 \times 10^{23} = 1.2 \times 10^{24}$ atoms.

Mole ⟷ gram

The molar mass (M) can be calculated from *the formula of the substance*, which is the mass of a substance per one mole particles (in $\text{g}\,\text{mol}^{-1}$). It allows us to convert between the mass and the amount of particles in moles.

The relationship between the amount in mol and mass in g is given by:



$$m = n \cdot M$$

m = mass [g]
n = chemical amount [mol]
M = molar mass [$\text{g}\,\text{mol}^{-1}$]

Example.

What is the amount in moles of $4.00\,\text{g}$ in NaOH?

$$M(\text{NaOH}) = 22.99 + 16.00 + 1.01 = 40.0\,\text{g}\,\text{mol}^{-1}$$
$$n = \frac{m}{M} = \frac{4.00\,\text{g}}{40.0\,\text{g}\,\text{mol}^{-1}} = 0.100\,\text{mol NaOH}$$

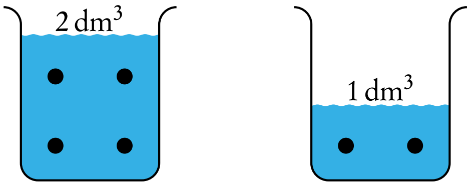
Mole ⟷ [concentration]

Solution a homogeneous mixture of a substance (the solute) dissolved in another substance (the solvent)

(Molar) concentration (C) is the amount of solute (in mol) per unit volume (in dm^3), often written using $[\dots]$, and expressed in $mol\,dm^{-3}$

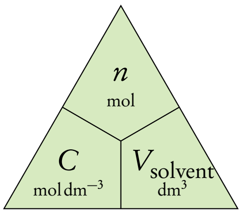
Standard solution a solution with a known concentration of solute

The solute concentration is independent of the solvent volume. When we dissolve 4 mol sugar in 2 dm^3 water, it has a particular 'sweetness'. This sweetness is a measure of the concentration of sugar in water. If we would poor out 1 dm^3 from the solution, it would still be equally sweet (same concentration) but only contain half the sugar content (half the amount in moles).



$$\frac{4\,mol}{2\,dm^3} = 2\,mol\,dm^{-3} \qquad \frac{2\,mol}{1\,dm^3} = 2\,mol\,dm^{-3}$$

The relationship between the amount in mol and concentration in $mol\,dm^{-3}$ is given by:



$$n = V_{solvent} \cdot C$$

n = chemical amount [mol]

$V_{solvent}$ = solvent volume [dm^3]

C = concentration [$mol\,dm^{-3}$]

Example.

What amount of NaCl (in moles) is required to prepare 250 cm^3 of a 0.200 $mol\,dm^{-3}$ solution?

$n = V_{solvent} \cdot C = 250\,cm^3 \cdot 0.200\,mol\,dm^{-3} = 50\,mmol$

Which solution contains the greatest amount (in mol) of solute?

		$V_{solvent}$	$\cdot C$	$= n$ in mol	
A.	10.0 cm^3 of 0.500 $mol\,dm^{-3}$ NaCl	10.0	·0.500	= 5 mmol	
B.	20.0 cm^3 of 0.400 $mol\,dm^{-3}$ NaCl	20.0	·0.400	= 8 mmol	
C.	30.0 cm^3 of 0.300 $mol\,dm^{-3}$ NaCl	30.0	·0.300	= 9 mmol	←
D.	40.0 cm^3 of 0.200 $mol\,dm^{-3}$ NaCl	40.0	·0.200	= 8 mmol	

It's very useful to remember that $cm^3 \cdot mol\,dm^{-3} = mmol$

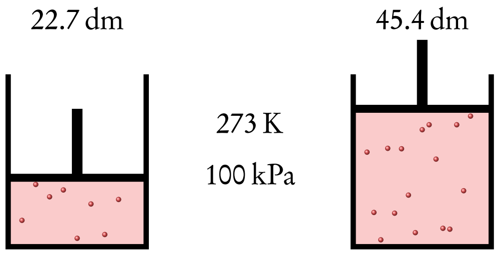
Mole ⟷ volume gas

Avogadro's law equal volumes of *all* gases, at the same temperature and pressure, have the same number of molecules

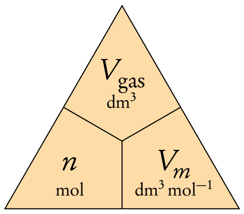
Molar volume (V_m) the volume of one mole gas, expressed in $\text{dm}^3\,\text{mol}^{-1}$ or $\text{m}^3\,\text{mol}^{-1}$, at a particular pressure and temperature.

Assuming the gas is an ideal gas, Avogadro's law is tested quite often: it should be understood that the molar ratio can be applied to gas volumes.

The volume of an ideal gas at constant temperature and pressure is proportional to the number of particles (in moles). So when twice the number of particles are placed into a cylinder, then the volume becomes twice as large. The volume of one mole gas (molar volume) at STP is $22.7\,\text{dm}^3\,\text{mol}^{-1}$.



The relationship between the amount in mol and gaseous volume in dm^3 is given by:



$$V_{\text{gas}} = n \cdot V_m$$

n = chemical amount [mol]
V_{gas} = gas volume [dm^3]
V_m = molar volume [$\text{dm}^3\,\text{mol}^{-1}$]

Example.

Calculate the volume of nitrogen gas produced by the decomposition of 2.50 mol of $NaN_3(s)$ at STP in the reaction $2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$.

Since the molar ratio $NaN_3 : N_2 = 2:3$, $\frac{2.50\,\text{mol}}{2} \times 3 = 3.75\,\text{mol}\ N_2$ forms.

At STP $V_m = 22.7\,\text{dm}^3\,\text{mol}^{-1}$, $V_{\text{gas}} = n \cdot V_m = 3.75 \cdot 22.7 = 85.1\,\text{dm}^3$

1.3.2 Gas laws and ideal gases

An ideal gas is a theoretical gas that assumes that: *the volume of particles is negligible* compared to the volume of the surrounding empty space, and *no kinetic energy is lost in the collisions between the particles*. Whether these assumptions are justified is outside the scope of the IB syllabus, so from now on we will treat all gases as ideal gases.

Pressure the force exerted by the collisions of particles on the walls of its container

$$\text{pressure at sea level} = 100\,\text{kPa} = 1.00 \times 10^5\,\text{Pa}$$

Temperature the average kinetic energy of particles

$$T_{\text{in K}} = T_{\text{in °C}} + 273 \qquad \text{and} \qquad T_{\text{in °C}} = T_{\text{in K}} - 273$$

STP standard temperature and pressure: 273 K and 100 kPa

SATP standard ambient temperature and pressure: 298 K and 100 kPa

The ideal gas law assumes ideal gas behaviour, and it is an equation that relates the pressure, volume, amount in moles and the temperature of a gas. Critically, SI units *must* be used in the ideal gas law:

$$PV = nRT$$

P = pressure [Pa]
V = volume [m^3]
n = amount of substance [mol]
R = ideal gas constant $8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
T = temperature [K]

Memorize the ideal gas law: $PV = nRT$. For paper 2 you will have it in the databook, but you will also need it for paper 1 questions!

Example.

Using the ideal gas law, verify that V_m at STP is $22.7\,\text{dm}^3\,\text{mol}^{-1}$.

Molar volume (V_m) = the volume (V) *per* mole (n), or $V_m = \dfrac{V}{n}$.

Rearrange the ideal gas law: $\dfrac{V}{n} = \dfrac{RT}{P} = V_m$

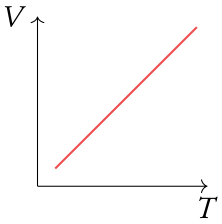
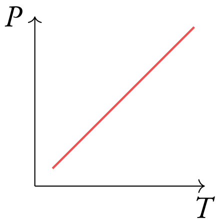
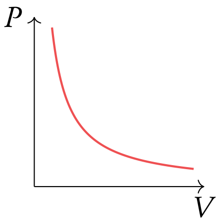
$$V_m = \frac{RT}{P} = \frac{8.31 \cdot 273\,\text{K}}{1.00 \times 10^5\,\text{Pa}} = 2.27 \times 10^{-2}\,\text{m}^3\,\text{mol}^{-1} = 22.7\,\text{dm}^3\,\text{mol}^{-1}$$

Questions involving the ideal gas law in paper 1 are often presented 'at constant mass'; this means that the number of moles n is kept constant. R is also a constant. Rearranging the ideal gas law with the variables to one side, and the constants to the other yields: $\frac{PV}{T} = nR$. Since only P, V and T are allowed to change, nR will remain constant. Mathmatically two situations ($_1$) and ($_2$) can be related by:

$$nR = \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Memorize this formula or how to derive it, because it will allow you to answer all questions regarding gas laws!

From $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ we can derive Boyle's law, Charles' law and Gay-Lussac's Law (and Wikipedia knows which is which). In each of the three gas laws, one of the quantities (P, V or T) is fixed, as well n ('at constant mass').

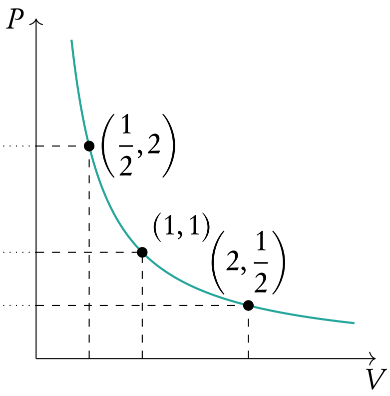
	constant pressure	constant volume	constant temperature
derivation of gas law	$\frac{\cancel{P_1} V_1}{T_1} = \frac{\cancel{P_2} V_2}{T_2}$ $\frac{V_1}{T_1} = \frac{V_2}{T_2}$	$\frac{P_1 \cancel{V_1}}{T_1} = \frac{P_2 \cancel{V_2}}{T_2}$ $\frac{P_1}{T_1} = \frac{P_2}{T_2}$	$\frac{P_1 V_1}{\cancel{T_1}} = \frac{P_2 V_2}{\cancel{T_2}}$ $P_1 V_1 = P_2 V_2$
relation	$V \propto T$	$P \propto T$	$P \propto \frac{1}{V}$
graph			

Example.

At constant temperature, sketch a diagram that shows how P changes when V changes.

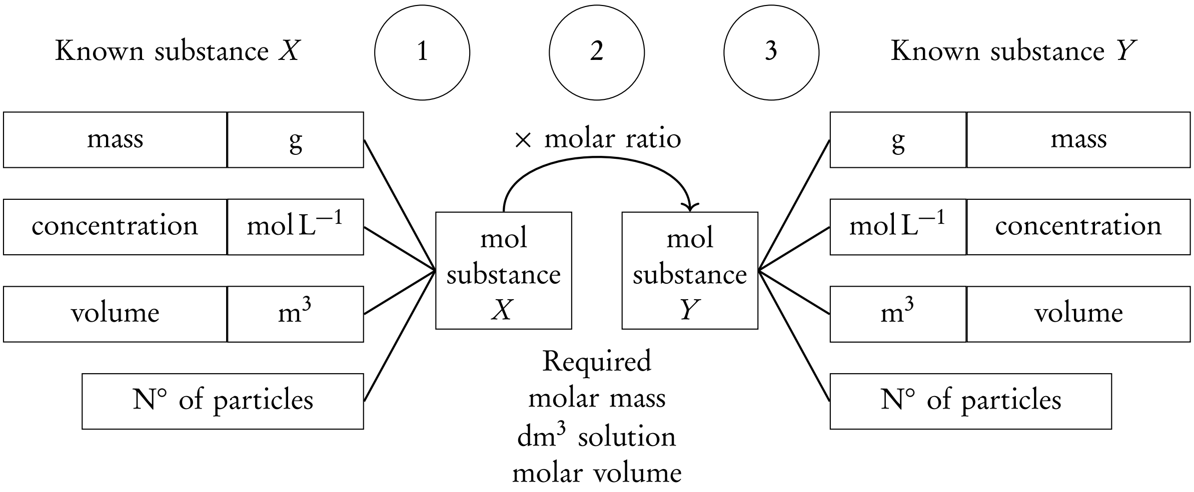
$P_1 V_1 = P_2 V_2$ holds, so put in some numbers to figure out the relation.
Assume $P_1 V_1 = 1 \cdot 1 = 1$:

$$P \times V = 1 = \text{constant}$$
$$2 \times \frac{1}{2} = 1 = \text{constant}$$
$$1 \times 1 = 1 = \text{constant}$$
$$\frac{1}{2} \times 2 = 1 = \text{constant}$$



1.3.3 Chemical calculations

The basics of all chemical calculations can be summarized as follows:



Performing chemical calculations

5.0 g of CH_4 undergoes complete combustion. Calculate the volume of the resulting gases under STP assuming that water forms as a gas.

1.	Note the reaction equation and list the information given	$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ 5.0 g CH_4
2.	Convert units to mole	$CH_4 M_m = 12.0 + 4 \cdot 1.01 = 16.04\,g\,mol^{-1}$ $\frac{5.0}{16.04} = 0.312\,mol\,CH_4$
3.	Use the molar ratio to convert to the number of moles of the substance(s) asked for	The volume of all the gases that form is required. Per 1 mol CH_4, 3 mol gas forms $0.312\,mol\,CH_4 \cdot \frac{3}{1} = 0.935\,mol$ gas.
4.	Convert moles to required units	Under STP $V_m = 24.5\,dm^3\,mol^{-1}$, $0.935\,mol \cdot 24.5\,dm^3\,mol^{-1} = 22.9\,dm^3$
5.	Check significant figures and units	Looking back to step 1 the amount of CH_4 is given in two significant figures, so the answer should also be written using two significant figures ⟶ $23\,dm^3$

Limiting and excess reactant

12 table legs and 4 table tops are stored in the warehouse of a table factory. Our intuition tells us that we cannot make 4 tables, since it would require 16 table legs. So even though more table legs are available than table tops, due to the ratio in which they are needed the table legs are the limiting reactant and the table tops are in excess. Doing chemistry we do not have the same intuition, but we perform the same math.

Theoretical yield the maximum quantity of product that can be obtained from given quantities of reactants, assuming completion

Limiting reactant the reactant that determines the theoretical yield of a product, after the reaction is complete there will be none left

Excess reactant the reactant that is not used up by the reaction, after the reaction is complete this substance will still be present

All calculations must be done using the amount of the limiting reactant, since it determines how much product will be made (i.e. the available 12 table legs determine that the theoretical yield of tables is 3).

Identify the limiting reactant

4.22 g Al reacts with 25.0 g Br_2 in the following reaction: $2Al + 3Br_2 \longrightarrow 2AlBr_3$. Identify the limiting reactant and use it to determine the theoretical yield of $AlBr_3$.

1. Convert units to moles

$$\frac{4.22\,g}{26.98\,g\,mol^{-1}} = 0.156\,mol\ Al$$

$$\frac{25.0\,g}{2 \cdot 79.90\,g\,mol^{-1}} = 0.156\,mol\ Br_2$$

2. Divide the number of moles of each reactant by its reaction coefficient. The reactant with the lowest result will be the limiting reactant.

$$\text{Al:}\frac{0.156\,mol}{2} = 0.078$$

$$\text{Br}_2\text{:}\frac{0.156\,mol}{3} = 0.052$$

So Br_2 is the limiting reactant.

3. Use the number of moles *of the limiting reactant* from step 1 and the molar ratio to calculate the number of moles of the requested substance

The molar ratio of $AlBr_3 : Br_2 = 2 : 3$, so

$$0.156\,mol \cdot \frac{2}{3} = 0.104\,mol\ AlBr_3$$

Percentage yield and atom economy

$$\text{Percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \cdot 100\%$$

The experimental yield is the amount that is actually produced. This is normally less than (and never more than) the theoretical yield due to losses caused by:

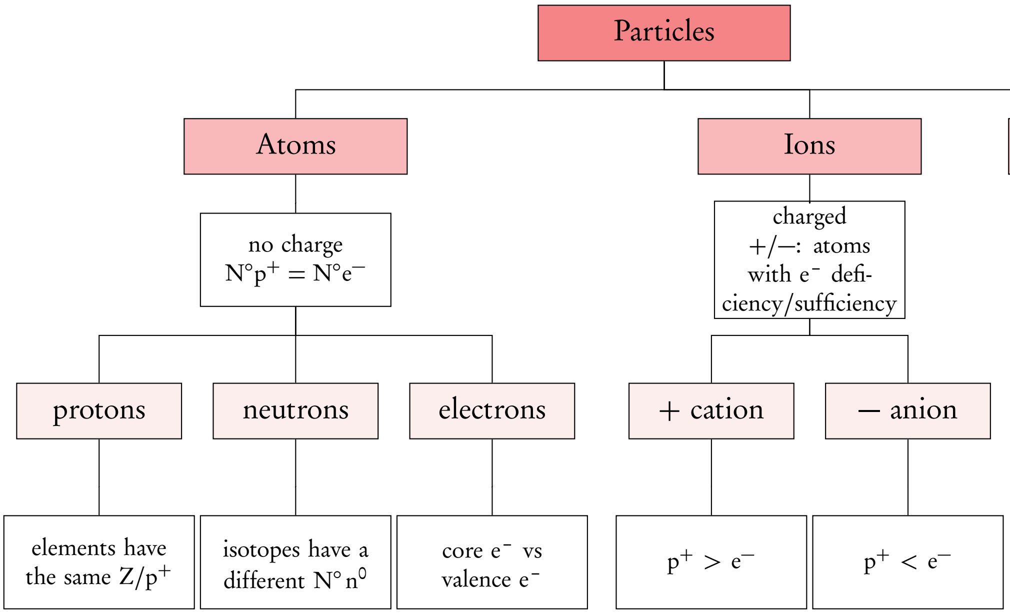
- Unwanted side reactions
- Incomplete reaction (e.g., equilibrium)
- Complete product separation/purification is impossible

$$\text{Atom economy} = \frac{\text{total mass of desired products}}{\text{total mass of all products}} \cdot 100\%$$

ATOMIC STRUCTURE

2

2.1 Types of particles



Atoms contain subatomic particles: protons, neutrons and electrons

Nucleus ⊕ protons and neutrons form the atom's nucleus

Electron cloud ⊖ electrons occupy the space outside the nucleus in shells/subshells/orbitals

	notation	mass	relative mass	charge	relative charge
proton	p^+	1.67×10^{-24} g	1 u	1.60×10^{-19} C	+1
neutron	n^0	1.67×10^{-24} g	1 u	0 C	0
electron	e^-	9.11×10^{-28} g	≈0 u	-1.60×10^{-19} C	−1

Atom charge = 0. the smallest constituent unit of ordinary matter that has the properties of a chemical element

anion: a negative ion

cation: is pawsitive

Ion charge $\neq 0$, so the number of $e^- \neq$ the number of p^+

Negative ion/anion ⊖ contains *more* e^- than p^+

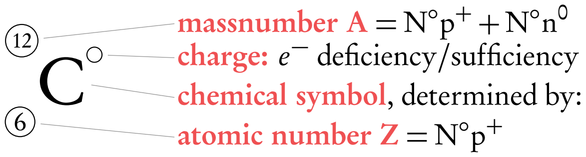
Positive ion/cation ⊕ contains *less* e^- than p^+

Element all atoms of the same element have the same number of p^+ (i.e. the same atomic number Z)

Isotopes have the same chemical properties, but different physical properties

Isotopes atoms of the same element but with a different number of n^0, resulting in a different mass number ^{A}X.

2.2 Notation



massnumber A $= N°p^+ + N°n^0$

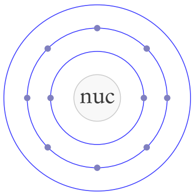
charge: e^- deficiency/sufficiency

chemical symbol, determined by:

atomic number Z $= N°p^+$

Example.

This atom has 8 p^+ and 10 n^0, what is the chemical notation for this ion?



$$\left.\begin{aligned} Z &= N°p^+ = 8 \\ A &= N°p^+ + N°n^0 = 8 + 10 = 18 \\ \text{charge} &= N°p^+ - N°e^- = 8 - 10 = -2 \end{aligned}\right\} {}^{18}_{8}O^{2-}$$

⊖ ions have extra e^-!

Find the symbol, Z, p^+, n^0, e^- for: ${}^{11}_{5}X$, ${}^{19}_{9}X^-$ and ${}^{27}Al^{3+}$

	Symbol and Z	N° p^+	N° n^0	N° e^-
${}^{11}_{5}X$	Z= 5, so B	5	$11 - 5 = 6$	5
${}^{19}_{9}X^-$	Z= 9, so F	9	$19 - 9 = 10$	$9 + 1 = 10$
${}^{27}Al^{3+}$	Al, so Z= 13	13	$27 - 13 = 14$	$13 - 3 = 10$

2.3 Isotopes: abundance and A_r

Relative atomic mass (A_r) the weighed mean of all the isotopes of one element and their natural abundances, relative to one atomic mass unit, which is $^1/_{12}$ of the mass of a ^{12}C atom

$$A_r = \begin{pmatrix}\text{fractional} \\ \text{abundance} \\ \text{of isotope 1}\end{pmatrix} \times \begin{pmatrix}\text{mass of} \\ \text{isotope 1}\end{pmatrix} + \begin{pmatrix}\text{fractional} \\ \text{abundance} \\ \text{of isotope 2}\end{pmatrix} \times \begin{pmatrix}\text{mass of} \\ \text{isotope 2}\end{pmatrix} + \ldots$$

$1\,\text{u} = 1\,\text{g}\,\text{mol}^{-1}$

Example.

Calculate A$_r$ of bromine, given that the abundancies of ^{79}Br and ^{81}Br are 50.69 % and 49.31 %.

$$\begin{aligned} A_r(\text{Br}) &= 50.69\,\% \cdot {}^{79}\text{Br} + 49.31\,\% \cdot {}^{81}\text{Br} \\ &= 0.5069 \cdot 79 + 0.4931 \cdot 81 \\ &= 79.90\,\text{g}\,\text{mol}^{-1} \end{aligned}$$

Calculate the abundancies of ^{69}Ga and ^{71}Ga, given these are the only stable isotopes of Ga and $A_r = 69.72\,\text{g}\,\text{mol}^{-1}$

Since ^{69}Ga and ^{71}Ga are the only stable isotopes we can say that:
fractional abundance ^{69}Ga + fractional abundance ^{69}Ga = 1(or 100 %)
If we let x = fractional abundance ^{69}Ga then fractional abundance ^{71}Ga $= 1 - x$

$$A_r(\text{Ga}) = x \cdot {}^{69}\text{Ga} + (1 - x) \cdot {}^{71}\text{Ga}$$

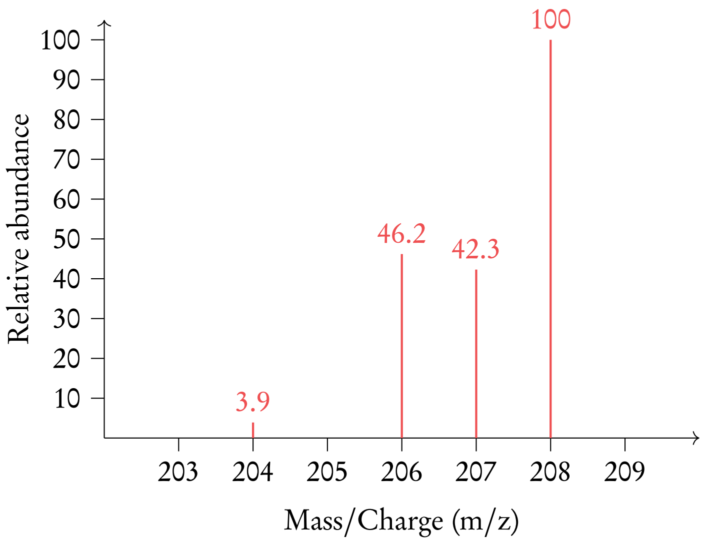
$$69.72\,\text{g}\,\text{mol}^{-1} = x \cdot 69 + (1 - x) \cdot 71 = 69x + 71 - 71x$$

$$x = 0.64$$

So the abundance of ^{69}Ga is 64 % and the abundance of ^{71}Ga is 100 % − 64 % = 36 %

Mass spectrometer

A mass spectrometer is an analytical instrument that can measure the mass of each isotope in a sample. So if a sample of lead, Pb, is injected into the device, the following spectrum and relative abundances will result:



Isotope	Relative abundance
^{204}Pb	3.9
^{206}Pb	46.2
^{207}Pb	42.3
^{208}Pb	100

The data of the mass spectrum allows us to calculate the average atomic mass by weighing the isotopic mass against its relative abundance. Note that the abundance is not given as a %, so we have to divide by the sum of all the relative abundances.

$$\mathrm{A_r\ (Pb)} = \frac{3.9 \cdot 204 + 46.2 \cdot 206 + 42.3 \cdot 207 + 100 \cdot 208}{3.9 + 46.2 + 42.3 + 100} = 207.2\,\mathrm{g\,mol^{-1}}$$

2.4 Atomic shells/subshells/orbitals

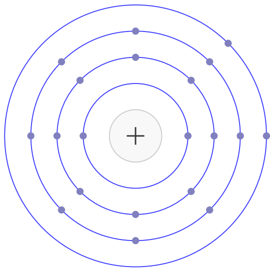
Electron shell $n = 1, 2, 3\ldots$ principal energy level which each contains $2n^2$ electrons, further divided in a number of subshells

Subshells s, p, d, f each subshell has a paricular number of orbitals, and each has its own geometry

Atomic orbital region with a specific geometry that can host two electrons of opposite spin

shell n	max. N° of e^- $2n^2$	N° of orbitals s	 p	 d	 f	 total	electron configuration
1	$2 \cdot 1^2 = 2$	1	—	—	—	1	$1s^x$
2	$2 \cdot 2^2 = 8$	1	3	—	—	4	$2s^x\ 2p^x$
3	$2 \cdot 3^2 = 18$	1	3	5	—	9	$3s^x\ 3p^x\ 3d^x$
4	$2 \cdot 4^2 = 32$	1	3	5	7	16	$4s^x\ 4p^x\ 4d^x\ 4f^x$

Electron shell is also often referred to as the *main energy level*

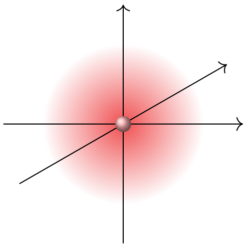


The principal electron shells can be imagined as an onion: the first shell ($n = 1$) is closest to the nucleus and each of the following shells is further away. The shells are numbered: $n = 1$, $n = 2$, …

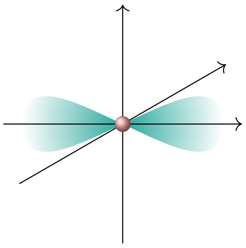
Every shell contains the s subshell, from the second shell ($n = 2$) forward all shells contain the p subshell, from the third shell ($n = 3$) all shells contain the d subshell etc.

The shape of the subshells

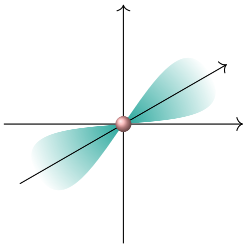
Every s subshell consist of one spherical orbital, which is further away from the nucleus the higher the shell number. The p subshell always contains 3 orbitals which are aligned along the xyz-axis. Since the second shell ($n = 2$) contains the 2s 2p subshells which can host 2 and 6 electrons respectively, the maximum total number of electrons in the second shell is 8.



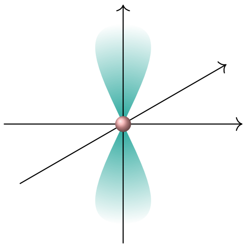
s orbital



p_x orbital



p_y orbital



p_z orbital

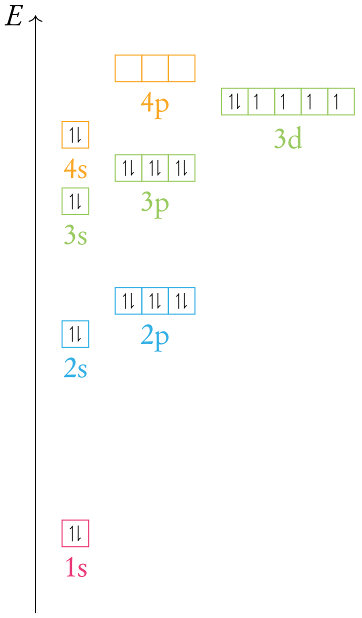
2.4.1 Electron configuration

Electron configuration shows the number of e^- in each subshell in the groundstate (the lowest energy state)

Aufbau Principle = 1s 2s 2p 3s 3p <u>4s 3d</u> 4p electrons are placed into orbitals with *lowest energy* first, which are not necessarily orbitals closest to the nucleus. Importantly: electrons occupy 4s before 3d orbitals.

Pauli's Exclusion Principle per orbital a maximum of 2 e^- with opposite spin are allowed.

Hund's rule instead of forming pairs in the same orbital, electrons rather occupy empty orbitals to minimize repulsion.



Write the electron configuration of atoms

Write the *full* and *condensed* electron configuration for Fe.

1.	Determine the total number of e^-	$_{26}$Fe, is an atom so: number of p^+ = number of e^- = 26
2.	Allocate each electron to each subshell according to the Aufbau principle. Place max. 2 e^- in the s subshells, max. 6 e^- in the p subshells, max. 10 e^- in d subshell.	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$ Abbreviated form: $[Ar]\ 4s^2\ 3d^6$

Note that when asked to write the *full electron configuration*, the condensed form is incorrect!

To write the electron configuration of ions, we have to add or remove electrons from the electron configuration of the atom equal to the charge of the ion. As the 3d sublevel becomes populated with electrons, the relative energies of the 4s and 3d fluctuate relative to one another and the 4s ends up higher in energy as the 3d sublevel fills. *This means that 4s electrons are removed prior to 3d electrons.*

Write the electron configuration of ions

Write the *condensed* electron configuration for Fe^{3+}

1.	Write the electron configuration *of the atom*	$[Ar]4s^2 3d^6$
2.	Add electrons / remove electrons from the outermost shell *(4 s before 3 d)*	Fe^{3+} has 3 fewer e^- than the atom. First remove two 4 s electrons, and then remove one 3 d electron: $[Ar]\,3d^5$

d^4 and d^9 exceptions

The situation when subshells are completely filled, or half-filled, is energetically favoured. An electron from the 4 s subshell can be promoted to attain a half-filled d-subshell (d^5) or full d-subshell (d^{10}).

	incorrect	correct
Cr	$[Ar]\,\cancel{4s^2}3d^4$	$[Ar]\,4s^1\,3d^5$
Cu	$[Ar]\,\cancel{4s^2}3d^9$	$[Ar]\,4s^1\,3d^{10}$

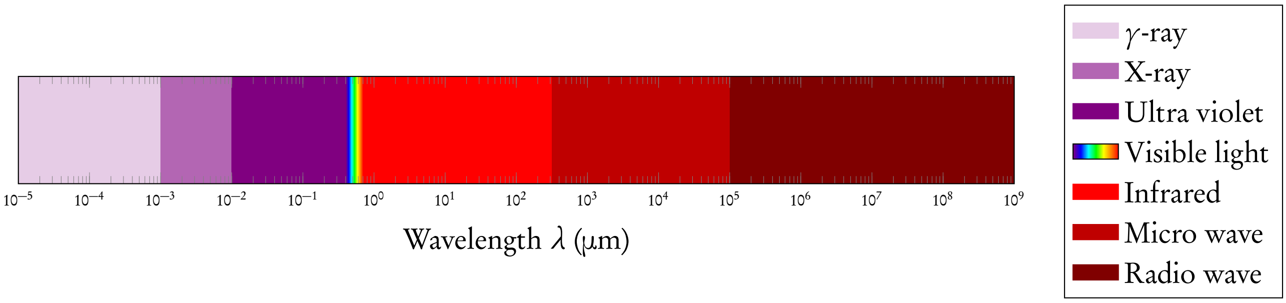
Memorize these two exceptions because they have been tested often!

2.5 Electromagnetic spectrum

Electromagnetic radiation a form of energy that propagates through space at the speed of light as electromagnetic waves, or photons

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

$$\begin{array}{lll} E_{\text{photon}} & = \text{energy of a photon} & [\text{J}] \\ h & = \text{Planck's constant} & 6.63 \times 10^{-34}\ \text{J s} \\ \nu \text{ or } f & = \text{frequency} & [\text{s}^{-1}] \\ \lambda & = \text{wavelength} & [\text{m}] \end{array}$$



Visible light (Vis) is an example of electromagnetic (EM) radiation. The colour of light is tied to the amount of energy of a photon. But visible light is only a small part of the EM spectrum; at the higher energy end of the spectrum we find ultraviolet (UV), X-ray and γ-ray, at the lower energy end of the spectrum we find infrared (IR), microwaves and radiowaves.

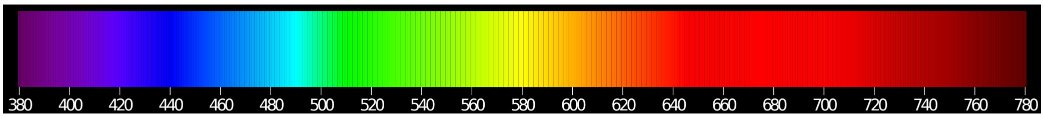
Electron energy levels

The energy level of an electron depends on which atomic orbital it occupies. The lowest energy level is called the groundstate; an electron can move to a higher energy level (excited state) by absorption of a photon. And similarly, an electron can move from an excited state to a lower energy level by emitting a photon.

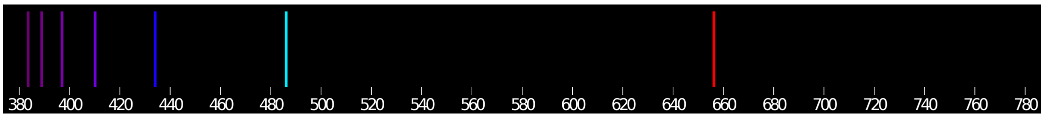
The transition between electron energy levels is only possible when the electron absorbs or emits a photon with exactly the same amount of energy as the difference between the energy levels. Energy transitions are discrete: of a particular amount of energy.

When excited electrons ‘fall’ from a higher to a lower energy state, photons with a dicrete amount of energy are emitted. The emission spectrum of atoms is a line spectrum: only light of a particular colour (discrete energy) is emitted.

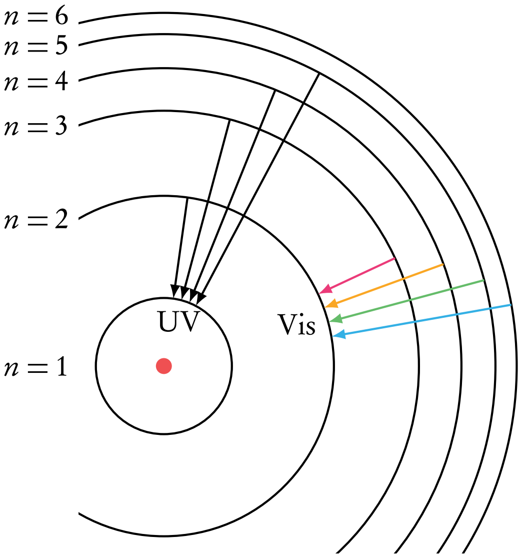
Continuous spectrum

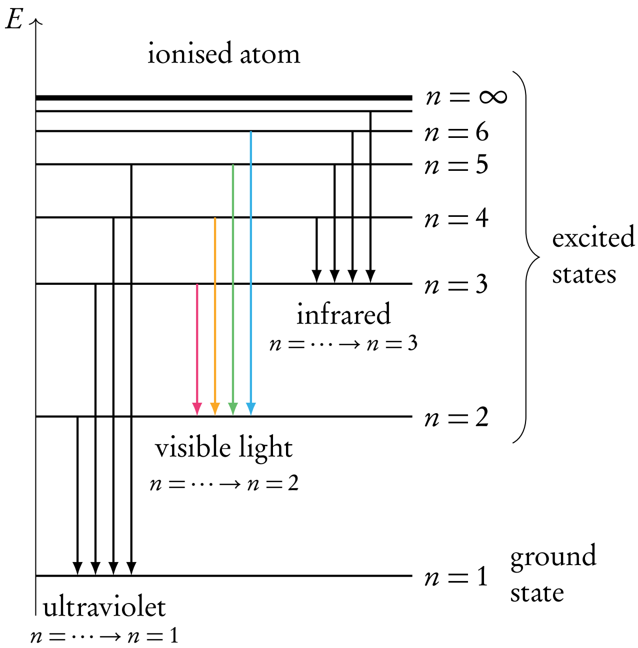


Hydrogen



Hydrogen energy levels



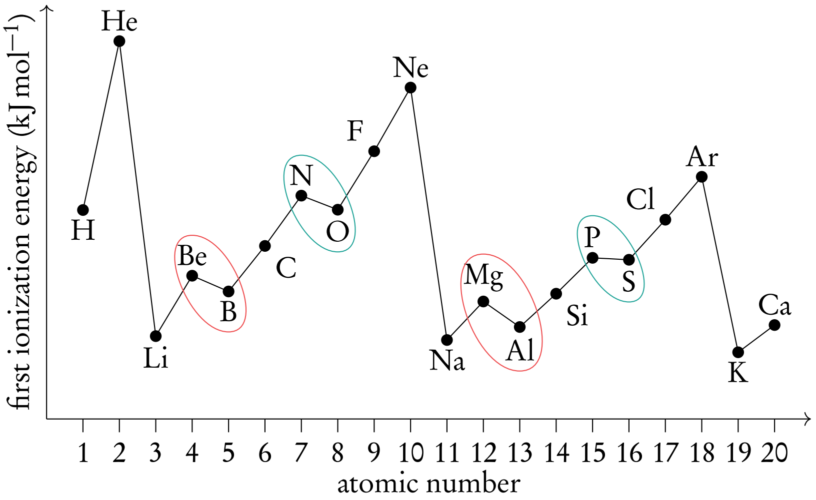


Electrons that 'fall' to the groundstate ($n = 1$) emit photons with the greatest amount of energy (UV radiation), because the length of the arrows is proportional to the amount of energy. Electrons that 'fall' to $n = 2$ emit visible light and to $n = 3$ emit infrared radiation.

Also note that the higher energy levels converge: the difference becomes smaller up to the point where the difference is 0. The electrons that 'fall' to $n = 2$, which are all photons of visible light, the energy difference between the *more energetic photons* is increasingly smaller. Line spectra indeed *converge at higher energy*.

2.6 Ionization energies

First ionization energy is the energy required to remove *one mole* of (the most loosely held) electrons from *one mole of gaseous atoms*, to produce one mole of gaseous ions each with a charge of 1+.



Evidence for shells

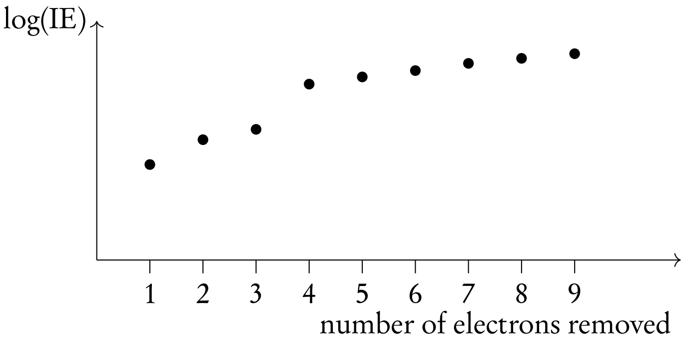
- **From He over Ne to Ar:** down the group it becomes easier to remove an electron since it is further away from the nucleus (in a higher shell).
- **From He to Li:** the first electron in a new shell is easily removed because the effective nuclear charge is low (+1), so it is weakly attracted.
- **From Li to Ne:** across a period it becomes harder to remove an electron since the effective nuclear charge increases, so the attraction increases.

Evidence for subshells

- **From Be [He]s^2 to B [He]s^2p^1:** an electron is added to the p-subshell, which has a slighly higher energy than the s-subshell, meaning it can be removed more easily.
- **From N [He]s^2p^3 to O [He]s^2p^4:** an electron is paired in a p-orbital causing increased repulsion, meaning it can be removed more easily.

Succesive ionisation energies

Note that y-axis is potted logarithmically, so abrubt changes in the y direction are compressed but are still easy to identify.



In the figure above we see the abrubt change occurring after the 3rd electron, which means that it is much harder to remove electron 4 than electron 3. All elements in group 13 (B, Al,Ga…) will have this characteristic, since after removing 3 electrons, removing the 4th will break the noble gas configuration.

3

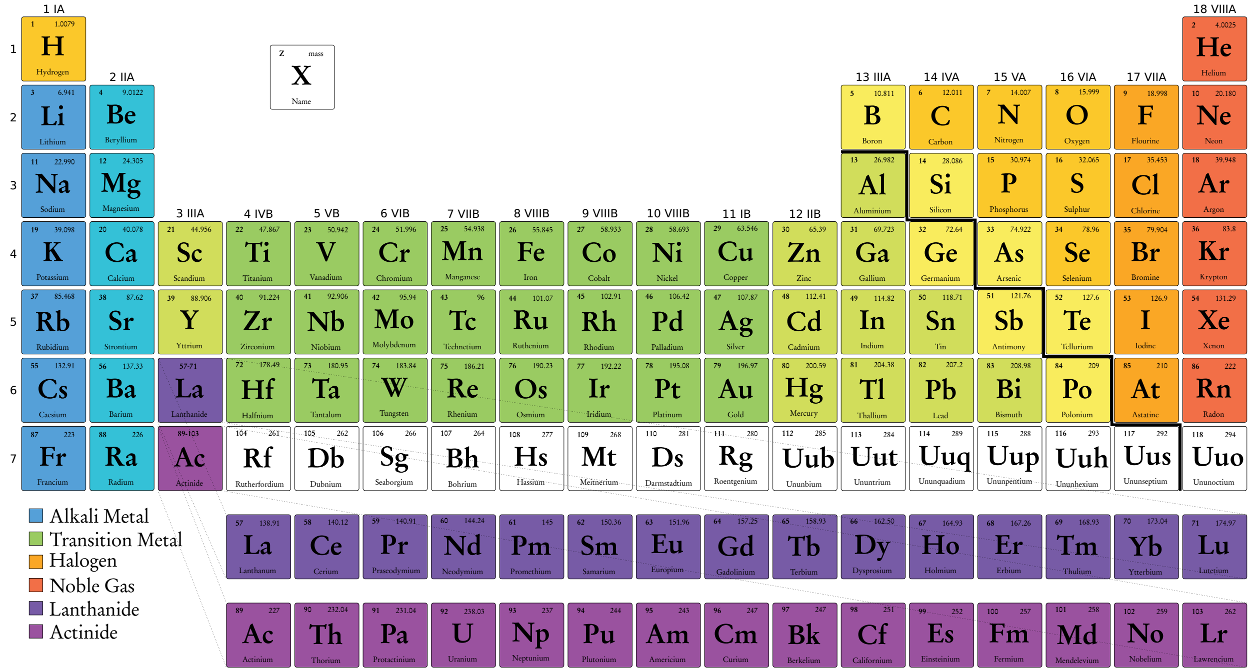
PERIODICITY

3.1 The Periodic Table (PT)

Period is a row in the periodic table, and it represents the principal electron shells ($n = 1, 2, \ldots$)

Group is a column in the periodic table, and it groups elements with similar chemical properties due to having the same number of valance e^-

Valence electrons are just the outermost electrons



Z mass
X
Name

	1 IA	2 IIA	3 IIIA	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H Hydrogen																	2 4.0025 He Helium
2	3 6.941 Li Lithium	4 9.0122 Be Beryllium											5 10.811 B Boron	6 12.011 C Carbon	7 14.007 N Nitrogen	8 15.999 O Oxygen	9 18.998 F Flourine	10 20.180 Ne Neon
3	11 22.990 Na Sodium	12 24.305 Mg Magnesium											13 26.982 Al Aluminium	14 28.086 Si Silicon	15 30.974 P Phosphorus	16 32.065 S Sulphur	17 35.453 Cl Chlorine	18 39.948 Ar Argon
4	19 39.098 K Potassium	20 40.078 Ca Calcium	21 44.956 Sc Scandium	22 47.867 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.693 Ni Nickel	29 63.546 Cu Copper	30 65.39 Zn Zinc	31 69.723 Ga Gallium	32 72.64 Ge Germanium	33 74.922 As Arsenic	34 78.96 Se Selenium	35 79.904 Br Bromine	36 83.8 Kr Krypton
5	37 85.468 Rb Rubidium	38 87.62 Sr Strontium	39 88.906 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 96 Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.42 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.71 Sn Tin	51 121.76 Sb Antimony	52 127.6 Te Tellurium	53 126.9 I Iodine	54 131.29 Xe Xenon
6	55 132.91 Cs Caesium	56 137.33 Ba Barium	57-71 La Lanthanide	72 178.49 Hf Halfnium	73 180.95 Ta Tantalum	74 183.84 W Tungsten	75 186.21 Re Rhenium	76 190.23 Os Osmium	77 192.22 Ir Iridium	78 195.08 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.38 Tl Thallium	82 207.2 Pb Lead	83 208.98 Bi Bismuth	84 209 Po Polonium	85 210 At Astatine	86 222 Rn Radon
7	87 223 Fr Francium	88 226 Ra Radium	89-103 Ac Actinide	104 261 Rf Rutherfordium	105 262 Db Dubnium	106 266 Sg Seaborgium	107 264 Bh Bohrium	108 277 Hs Hassium	109 268 Mt Meitnerium	110 281 Ds Darmstadtium	111 280 Rg Roentgenium	112 285 Uub Ununbium	113 284 Uut Ununtrium	114 289 Uuq Ununquadium	115 288 Uup Ununpentium	116 293 Uuh Ununhexium	117 292 Uus Ununseptium	118 294 Uuo Ununoctium
				57 138.91 La Lanthanum	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 145 Pm Promethium	62 150.36 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
				89 227 Ac Actinium	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237 Np Neptunium	94 244 Pu Plutonium	95 243 Am Americium	96 247 Cm Curium	97 247 Bk Berkelium	98 251 Cf Californium	99 252 Es Einsteinium	100 257 Fm Fermium	101 258 Md Mendelevium	102 259 No Nobelium	103 262 Lr Lawrencium

- 🟦 Alkali Metal
- 🟩 Transition Metal
- 🟧 Halogen
- 🟥 Noble Gas
- 🟪 Lanthanide
- 🟪 Actinide

Element type

Metals the majority of elements (in the figure: from blue to green), found on the left in the PT.
Non-metals form mostly molecules, (in the figure: from orange to red), found on the right in the PT.
Metalloids have intermediate properties

The division between elements that are metals and non-metals starts between Al (which is a metal) and B, and staircases down to the right. Later on it will be assumed knowledge and it is crucial to quickly tell if an element is metallic or not.

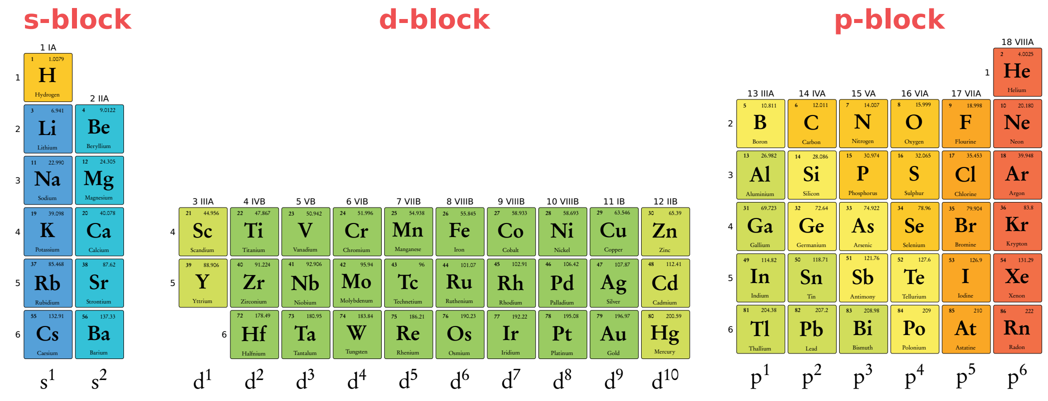
If you have never heard of the element, chances are that it's a metal.

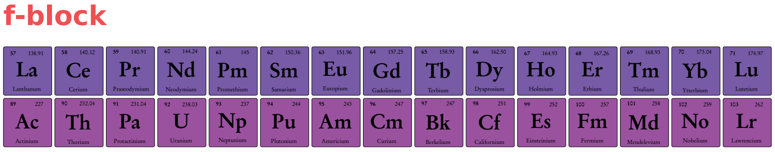
Subshells & blocks

The elements in the periodic table can be divided into four blocks, based on their electronic configuration. Since elements down a group have the same number of valence electrons, they will also have the same outermost subshell configuration.

Take the alkali metals for example: each has a single electron in the outermost shell, but each in a shell further away. The electron configurations of Li, Na and K are [He] $2s^1$, [Ne] $3s^1$ and [Ar] $4s^1$ respectively. The shell number that contains those electrons can be read off from the period number.

Note that H has the s^1 configuration but is not a metal, and He has s^2 configuration so we could consider placing it in above Be. But since the valence shell of He is completely full its properties correspond much closer to the noble gases.





The elements in the first row are called lanthanides, and in the second row actinides.

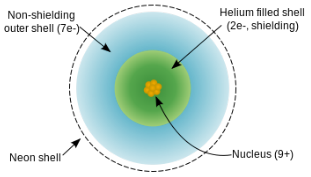
3.2 Periodic trends

Periodic trends are governed by the balance between attractive and repulsive electrostatic forces between the nucleus and the valence electrons.

Shielding electrons in lower *full* electron shells reduce the $\oplus$-charge that the valence electrons experience

Effective nuclear charge (Z_{eff}) the net $\oplus$ charge that valence electrons experience.

$$Z_{\text{eff}} = Z - \text{N}^{\circ}\text{shielding electrons}$$



$$Z_{\text{eff}} = 9 - 2 = +7$$

The nucleus of fluorine has a charge of 9+, the 1^{st} shell is full, reducing the effective attractive power of the nucleus to the valence electrons to 7+.

Example.

Determine the effective nuclear charge (Z_{eff}) for O, F, and Cl

${}_{8}\text{O}$ $1s^2\ 2s^2\ 2p^4$, it has 2 e^- in the filled 1st shell (shielding).

$$Z_{\text{eff}} = Z - \text{N}^\circ \text{ shielding electrons } = 8 - 2 = +6$$

${}_{9}\text{F}$ $1s^2 2s^2 2p^5$, so 2 e^- in the filled 1st shell (shielding).

$$Z_{\text{eff}} = Z - \text{N}^\circ \text{ shielding electrons } = 9 - 2 = +7$$

${}_{17}\text{Cl}$ $1s^2 2s^2 2p^6 3s^2 3p^5$, so 10 shielding electrons ($2 + 8e^-$ in the 1st and 2nd shells).

$$Z_{\text{eff}} = Z - \text{N}^\circ \text{ shielding electrons } = 17 - 10 = +7$$

Notice how the number of shielding e^- does not change across the period!

Notice how Z_{eff} does not change down a group!

The valence electrons experience an attractive force to the nucleus proportional to:

The effective nuclear charge (Z_{eff}) The higher the effective nuclear charge, the stronger the valence electrons are attracted to the nucleus. The effective nuclear charge increases → a period.

The distance The further away the valence electron is from the nucleus, the weaker it is attracted. The distace between the valence shell and the nucleus increases with increasing shell number, so ↓ a group.

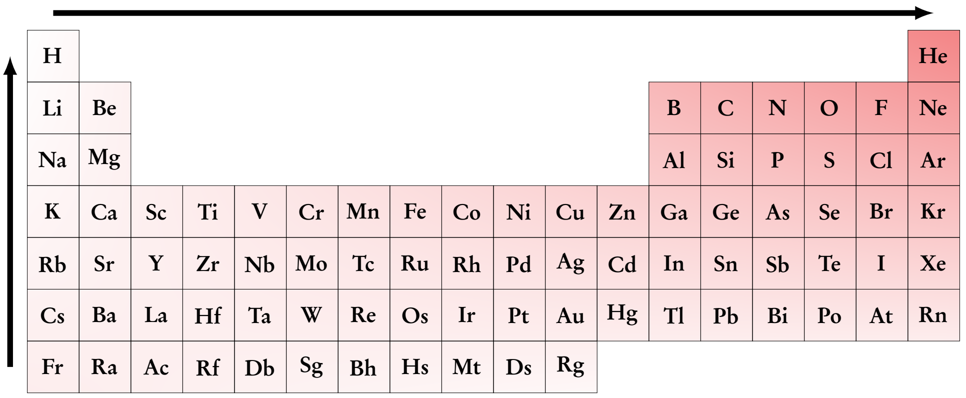
The valence electrons mutually repel each other. This repelling force increases when there are more electrons in the valence shell.

Comparatively, the effect of the attractive forces is stronger than the repelling forces, which means that only when the effective nuclear charge and the shell stays the same do we use arguments based on the repelling forces between valence electrons (ions).

To summarize, attraction between the ⊕ nucleus and the ⊖ valence electrons *increases*:

→ **the period** Z_{eff} increases, causing the valence electrons to experience stronger attraction to the nucleus. The valence shell number is the same, so the electrons are at the same (approximate) distance.

↑ **the group** e^- are closer to the nucleus, causing the valence electrons to experience stronger attraction to the nucleus. The Z_{eff} stays the same in the same group.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							

Attraction ↑ (between the nucleus and the valence e^-)

→ a period, because Z_{eff} increases (larger charge difference)
↑ a group, because distance decreases (larger distance difference)

Atomic radius the distance from the nucleus to the valence electron(s).

- When attraction ↑, the atomic radius ↓.

Ionic radius the distance from the nucleus to the valence electron(s).

Z_{eff} and the shell number stay the same, so the attraction stays the same. Only the repelling forces between the valence e^- changes:

- In ⊕ ions a number e^- are removed. All things equal, the mutually repelling forces between valence electrons decreases. *The larger the ⊕ charge, the smaller the ion.*
- In ⊖ ions a number of e^- are added. All things equal, the mutually repelling forces between valence electrons increases. *The larger the ⊕ charge, the larger the ion.*

The effect of adding or removing one electron while the attraction remains equal is significant. It's safe to assume that + ions are always smaller than atoms, and - ions always larger.

Electronegativity a measure of the ability of an atom to attract e^- in a covalent bond, i.e. loosely how greedy an element is for electrons

- When attraction ↑, the electronegativity ↑.

First ionization energy the energy change when one mole electrons are removed from one mole *gaseous atoms*, forming one mole *gaseous 1+ ions*

- When attraction ↑, the first ionization energy ↑.

First electron affinity the energy change when one mole of *gaseous atoms* acquire one mole electrons, forming one mole *gaseous 1- ions*.

- When attraction ↑, the first electron affinity ↑.

The energies of the first ionisation energy and electron affinity both increase when the attraction increases: it either requires more energy to remove the electron or releases more when it's acquired.

Example.

Order Ne, F^- and Na^+ in decreasing size. Explain why these are *isoelectronic*.

In order to compare the sizes of atoms and ions they have to be **isoelectronic:** i.e. have the same electron configuration. In this case, each has the [Ne] electronic configuration, but a different number of p^+ attracting the same number of e^-. The ⊖ ion will be largest, then the atom, then the ⊕ ion.

Answer: $Na^+ < Ne < F^-$ or $F^- > Ne > Na^+$

Read: Na^+ is *smaller than* Ne is *smaller than* F^-, or the reverse

Melting and boiling points

Alkali metals metallic bond strength increases when the *charge density* increases: smaller atoms with more valence electrons. The number of valence electrons is the same for the alkali metals, and charge density increases with smaller atoms. Liis predicted to have the highest MP and BP.

Halogens are apolar molecules with only London dispersion forces between them, which increase with increasing molecular mass. I_2 is predicted to have the highest MP and BP.

The melting and boiling points (MP and BP) of compounds critically depend on the bond strength between the particles, so this section should be understood after bonding is introduced.

Chemical reactivities

Alkali metals all contain 1 electron in their valence shell (s^1); in order to attain the noble gas configuration these elements react by *donating* an electron. The easier it is to remove the electron, the more reactive the element. Cs is most reactive and Li least, since all other things equal the e^- in Cs is furthest away from the nucleus.

Halogens all contain 7 electrons in their valence shell (s^2p^5); in order to attain the noble gas configuration these elements react by *accepting* an electron. The stronger the attractive force to electrons, the more reactive the element. F_2 is most reactive and I_2 least, since all other things equal the e^- in F_2 are closer to the nucleus.

Although the more reactive alkali metals and halogens will react more vigorously, they will undergo the same chemical reactions. You have to learn some of these reactions by heart, but fortunately all alkali metals and halogens undergo the same reactions and so they are interchangeable.

Type	Equation	
Alkali metals + water	$2\,Li_{(s)} + 2\,H_2O_{(l)} \longrightarrow 2\,LiOH_{(aq)} + H_{2(g)}$ $2\,Na_{(s)} + 2\,H_2O_{(l)} \longrightarrow 2\,NaOH_{(aq)} + H_{2(g)}$ …	forms alkaline solutions and H_2 which can combust (violently)
Alkali metals + halogens	$2\,Na_{(s)} + Cl_{2(g)} \longrightarrow 2\,NaCl_{(s)}$ $2\,K_{(s)} + F_{2(g)} \longrightarrow 2\,NaCl_{(s)}$ …	forms ionic halides, more reactive alkali metals + more reactive halogens produce a more vigorous reaction
Displacement reactions	$2\,KBr_{(aq)} + Cl_{2(aq)} \longrightarrow 2\,KCl_{(aq)} + Br_{2(aq)}$	the more reactive halogen displaces the ions of the less reactive halogen
Ionic reactions	$\left\{\begin{array}{l} 2\,Br^-_{(aq)} + Cl_{2(aq)} \longrightarrow 2\,Cl^-_{(aq)} + Br_{2(aq)} \\ 2\,I^-_{(aq)} + Cl_{2(aq)} \longrightarrow 2\,Cl^-_{(aq)} + I_{2(aq)} \\ 2\,I^-_{(aq)} + Br_{2(aq)} \longrightarrow 2\,Br^-_{(aq)} + I_{2(aq)} \end{array}\right.$	

Table 3.1: Reactions involving Halogens and Alkali Metals

3.3 Transition elements

Transition elements elements that have a common oxidation state (ion) that contains a partially filled d-subshell. Ions of transition elements have characteristic properties due to thier partially filled d-subshell.

Sc and Zn, though part of the d-block, are not transition metals. The common oxidation states Sc^{3+} and Zn^{2+} do not have a partially filled d-subshell. Instead, Sc^{3+} has no electrons in the d-subshell and Zn^{2+} has a completely filled d-subshell.

Electron configuration			
atom		ion	
Sc	$[Ar]4s^2 3d^1$	Sc^{3+}	$[Ar]$
Zn	$[Ar]4s^2 3d^{10}$	Zn^{2+}	$[Ar]3d^{10}$

The result is that these elements do not show the characteristic properties of transition metals that arise from their partially filled d-subshell.

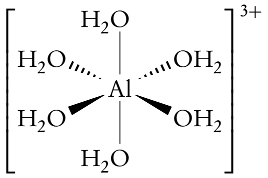
Variable oxidation states

Every transition metal can form ions with charge +2 owing to the fact that 4s electrons are lost before any 3d electrons. But many of the transition metals can also occur in other oxidation states: e.g. Fe^{2+} and Fe^{3+}, Cu^{+} and Cu^{2+}.

Complex ions

Complex ion a number of ligands form dative covalent bonds to a positive ion

Ligand a molecule or anion that donates a non-bonding pair of electrons to form a dative covalent bond with a metal ion



Coordination number the number of ligands around the central ion

Most of the transition metal ions and some non-transition metal ions form hexahydrated complexes in water, such as $[Al(H_2O_6]^{3+}$. Six water molecules donate one electron pair each, forming six dative covalent bonds. By applying the VSEPR theory from the next chapter, the central ion is surrounded by 6 electron domains so these complexes with a coordination number of 6 have an octahedral geometry.

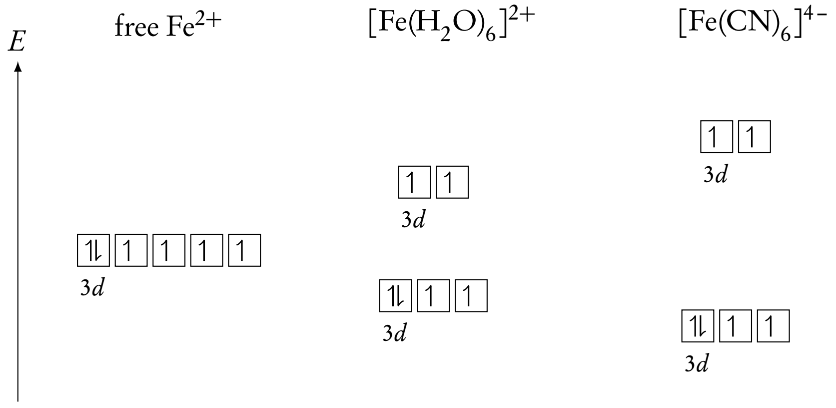
Complexes do not only form between ions and water molecules, but can form with many other substances so long as the ligand can donate an electron pair (lewis base). E.g. ammonia readily displaces water ligands, because it can form stronger dative covalent bonds than water.

The order of ligand bond strength is called the spectrochemical series:

$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CN^-$$

3.3.1 Partially filled d-subshell

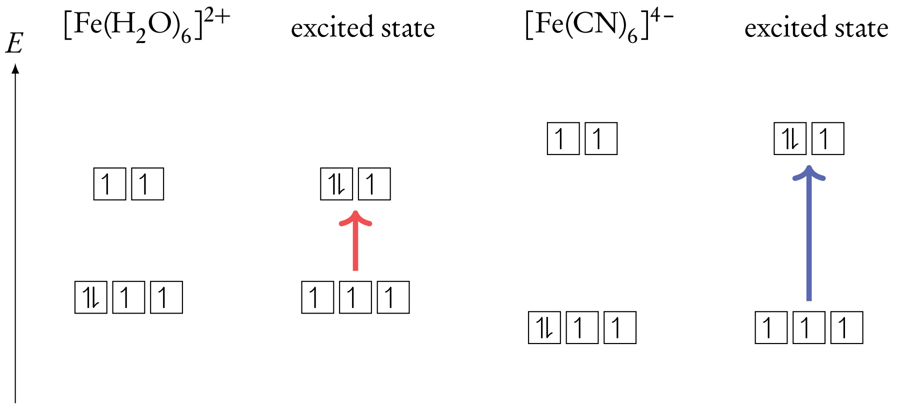
In a free ion, the energy levels of each of the 5 d-orbitals are the same, they are said to be degenerate. But when bonds with a particular geometry form such as described above, the d-electrons closer to the ligands will have a higher energy than those further away, which results in the d-orbitals splitting in energy. This splitting is what gives transition metals their characteristic properties.



Colour of transition metal complexes

In the previous chapter it was shown that electrons can absorb light, thereby moving into an excited state. When light is absorbed, an electron moves from a d-orbital with lower energy to a d-orbital with higher energy. The energy difference between the split d-orbitals is typically in the range of visible light.

Note that an electron, represented by ↿ and ⇂, moved from a d-orbital with lower energy to a higher energy d-orbital



So while $[Fe(H_2O)_6]^{2+}$ may absorb red photons, $[Fe(CN)_6]^{4-}$ will absorb photons with more energy such as blue light, because the energy levels are split further apart. The colour that is observed is the complementary colour to the light that is absorbed, so a solution containing $[Fe(H_2O)_6]^{2+}$ will appear green.

The colour of light absorption (i.e. the amount of splitting of the d-orbitals) thus depends on the identity and oxidation state of the central ion, the identity of the ligand and the coordination number / geometry around the central ion.

Magnetic properties of transition metals

When orbitals are partially filled, often (some of) the electrons in the orbitals are unpaired. Each electron has a spin, which when two electrons are paired cancel each other out. When electrons are unpaired each produces a tiny magnetic field. When those spins line up in a material they can produce a substantial magnetic field.

4

BONDING

The most stable electron configuration for each element is when the valence (= outermost) shell is completely occupied; this is known as the noble gas configuration. In order to attain the noble gas configuration atoms will share e^- (in covalent and metallic bonds) or exchange e^- (forming ions, and ionic bonds).

Depending on which element types combine we can predict the type of bonding:

substance

metal	ionic compound	molecular compound
only metal elements	metal + nonmetal elements	only nonmetal elements

Electrostatic / coulombic forces the attractive and repelling forces between charges.

Charge density the ratio between the charge of a particle compared to its size. The greater the charge density is, the greater the electrostatic attraction. Charge density increases when:

- the charge of the ions is greater, or when metals have more delocalized electrons,
- the distance is smaller between the charges (smaller atoms/ions).

When whole charges attract, such as between ions, the electrostatic forces will be *strong*; and when partial charges attract, such as between δ^- and δ^+, the electrostatic forces will be *weak*

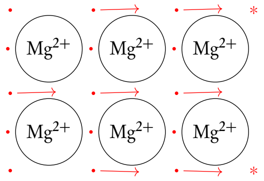
This chapter explores how some macroscopic (physical) properties of a substance are a consequence of how the particles are arranged and attract (microscopic properties):

melting point (MP) & boiling point (BP): increases as bond strength between the particles increases
solubility: like dissolves like
conduction: requires *charged particles* that *can move* to carry current.
malleability / ductility: depends on how well the substance can adapt to a change in the orientation of its particles.

4.1 Metallic Bonding

The valence electrons of metal atoms become detached from individual atoms forming a "sea of delocalised electrons", which can move freely through the lattice of metal nuclei.

Metallic bond the attraction due to the attraction of ⊕ metal nuclei to the delocalised "sea of electrons" ⊖ that moves freely



4.1.1 Properties of metals

Bond strength: MP & BP

The MP/BP of metals are high because metallic bonds are typically strong, due to the electrostatic attraction between ⊕ metal nuclei and ⊖ free electrons.

Variation among metals depends on charge density, which increases:

- when a metal has *more delocalised electrons*, and
- with *smaller size* of the metal atoms.

Metal	Delocalised e^-	Radius	MP
Mg	2	140 pm	650 °C
Na	1	160 pm	98 °C
K	1	227 pm	64 °C

Solubility

Metals *only* dissolve in other metals, to form *alloys*.

Many sources incorrectly state that some metals *dissolve* in acid. Instead, the metal *reacts* with the acid in a redox reaction in which the metal is converted into the metal cation, which is soluble in water:

$$\mathrm{M(s)} \longrightarrow \mathrm{M^{x+}(aq)} + \mathrm{xe^-}$$

Conduction

All metals can conduct electricity: since metals contain *charged particles*: the 'sea of delocalised electrons' that *can move freely*. The positive metal 'ions' cannot move in the metallic lattice.

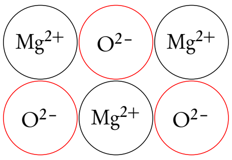
Malleability / ductility

When metals are reshaped, the positive ions in the metallic lattice slide over each other. The 'sea of electrons' adapts to the different orientation, maintaining the metallic bonds.

In alloys, the presence of foreign metal atoms disturb the host metal lattice structure, causing it to become harder to slide over each other. Alloys are less malleable.

4.2 Ionic bonding

Ionic bonds the attractive electrostatic forces between ions of opposing charge, holding ions in a lattice



4.2.1 Properties of ionic compounds

Bond strength: MP & BP

The MP/BP of ionic compounds are high because ionic bonds are typically strong, due to the electrostatic attraction between ⊕ cations and ⊖ anions.
Variation among ionic compounds depends on charge density, which increases:

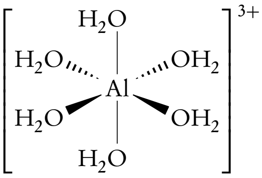
- when the ionic *charge is larger*, and
- with *smaller size* of the ions.

Solubility

In order to dissolve ionic compounds, the ionic bonds in the lattice between the ions have to be broken *and replaced* by stronger solvation bonds. The easier the ionic bonds are broken, and the stronger the solvation bonds are, the more soluble the ionic compound is.

Solvation solute ions are surrounded by a concentric shell of solvent molecules, forming solvation complexes

Hydration is solvation by water molecules



In solution, *conduction is proportional to the concentration of ions.*

Conduction

All ionic compounds contain ions, which are *charged particles*. But ions in a solid (s) lattice cannot move, and so not conduct electricity. Only when the ionic compound is liquid (l) or dissolved (aq) can the ions move freely, to conduct electricity.

Malleability

When one row of ions in the ionic lattice moves over 1 place with respect to another row, then all attractive forces between ions of opposing charge become repelling forces between ions of the same charge. This leads to a crack in the material, meaning that ionic compounds are brittle.

4.2.2 Ionic compounds

Ionic compound positive metal ions and negative non-metal ions form a strong lattice. Ionic compounds are charge neutral, so the empirical formula of ionic compounds balances the amount of positive and negative ions.

Writing the empirical formula for ionic compounds involves balancing the total number of positive and negative charges. Individual ions have a charge, while ionic compounds as a whole are neutral. The formula of ionic compounds is written as the smallest ratio between ions (empirical formula) so that the net charge is neutral (e.g., Na_2O).

Polyatomic ions ions containing more than one element

Ammonium:	NH_4^+	Nitrite:	NO_2^-
Acetate:	CH_3COO^-	Carbonate:	CO_3^{2-}
Cyanide:	CN^-	Sulfate:	SO_4^{2-}
Hydrogen carbonate:	HCO_3^-	Sulphite:	SO_3^{2-}
Hydroxide:	OH^-	Phosphate:	PO_4^{3-}
Nitrate:	NO_3^-		

Momorize the names and formulae of the polyatomic ions by heart!

Write empirical formula of ionic compounds

Write the ionic formula of aluminium sulphite

1.	Write down the individual ions (from memory!)	Al^{3+} and SO_3^{2-}
2.	Determine the smallest possible ratio of combining the ions to form a neutral compound. Trick: cross multiply the charges	charges $3+$ and $2-$, so $2 \times 3+$ and 3×-2
3.	Write the ionic formula, ratio in subscript. Put brackets $(\cdots)$ around polyatomic ions if more than 1. *Do not* put charges!	$Al_2(SO_3)_3$ using brackets around SO_3^{2-} because there is more than one

4.3 Covalent bonding

4.3.1 Nature of covalent bonding: "shared electron pair"

In molecules, non-metal atoms share electrons to achieve the noble gas configuration.

Hydrogen has one electron in its outer shell, so it needs one more in order to achieve the He noble gas configuration. Two hydrogen atoms form a *single covalent bond*: they both donate their 1 available valence electron to form a single shared pair. The shared pair of electrons lies in the region between the two nuclei and is attracted to them both.

While hydrogen achieves the noble gas configuration with 2 electrons in its outer shell, other non-metal atoms require 8 e^- in their valence shell to achieve the noble gas configuration. To determine bonding of those elements we use the octet rule.

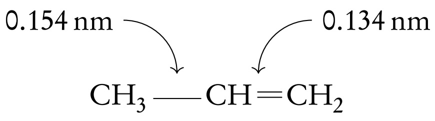
Bond strength

Covalent bonds form due to the electrostatic attraction of two ⊕ atomic nuclei to a shared electron pair, and since the electrostatic attraction between whole charges is strong, covalent bonds are also strong bonds (on par with metallic and ionic bonds).

In Table 4.1 the bond strengths and lengths of single, double and triple bonds are compared. Stronger bonds are shorter. Note that a double bond is *not quite* twice as strong as a single bond.

Table 4.1

		Bond energy		Length
Single	C—C	346 kJ mol^{-1}		0.154 nm
Double	C=C	614 kJ mol^{-1}	+268	0.134 nm
Triple	C≡C	839 kJ mol^{-1}	+225	0.120 nm



$CH_3—CH=CH_2$

Nomenclature of molecular compounds

I The number of atoms is prefixed by a Greek numeral prefix.
1. mono 2. di 3. tri 4. tetra 5. penta

II The most electronegative atom is written lastly and is suffixed by *-ide*.

Example.

Molecular formula	Systematic name	Trivial name
HCl	hydrogen chloride	hydrochloric acid
H_2O	dihydrogen oxide	water
CO_2	carbon dioxide	
CO	carbon monoxide	
PBr_3	phosphorus tribromide	
S_2Cl_2	disulfur dichloride	
N_2O_4	dinitrogen tetroxide	

The nomenclature of hydrocarbons (molecular compounds based on C and H) is very different, and will be discussed in chapter 10.

4.3.2 Lewis structures

Bonding electron pair pair of valence electrons that are shared between atoms (involved in a covalent bond).

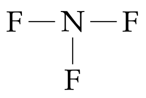
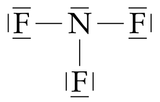
Non-bonding electron pair / lone pair pair of valence electrons that are not shared between atoms.

Only line notation is used in this study guide

Lewis structures shows all valence electrons on every atom, bonding *and* non-bonding, using either lines, crosses, dots or a combination

Octet rule the tendency of atoms to form a stable arrangement of eight electrons in their outer shell =surrounded by 4 e^--pairs

Using the octet rule we can draw the lewis structure of simple molecules very easily:

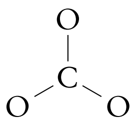
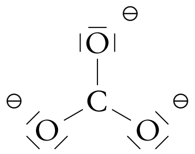
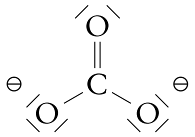
How to draw Lewis structures	Draw the Lewis structure of nitrogen trifluoride (NF_3)
1 → Calculate the number of valence electrons (add or subtract e^- for negative or positive charge)	$5 + 3 \cdot 7 = 26\,ve^-$
2 → Draw the *likely* structure of the molecule	
3 → Use non-bonding electron pairs to create octets (4 e^--pairs around each atom, except H and B)	
4 → Create double bonds if the number of ve^- are insufficient to create octets around every atom	✓ Every atom has an octet

Resonance structures/mesomerism

When multiple Lewis structures can be drawn that satisfy the above rules, electrons are delocalised which contributes to the stability of a molecule or polyatomic ion.

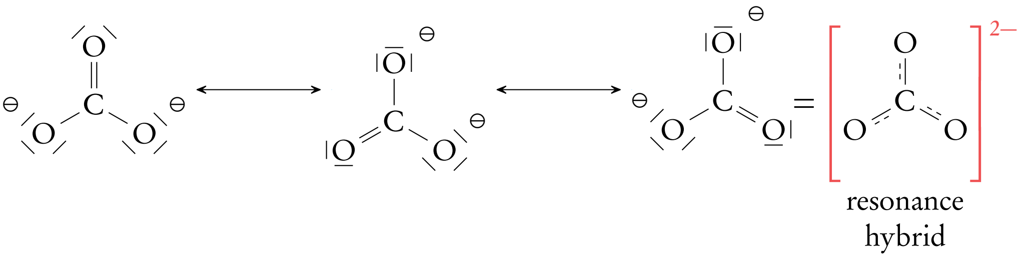
Example.

Draw the resonce structures and the resonance hybrid of CO_3^{2-}.

1 → The number of valence electrons: $C = 4$, $O = 6$, and two additional electrons due to the charge.	$4 + 3 \cdot 6 + 2 = 24\,ve^-$ or 12 e^--pairs
2 → Likely structure	
3 → Place the remaining 9 e^--pairs on the outermost atoms	
4 → Create a double bond by removing one non-bonding pair	

Example.

In step 4 the placement of the double bond on any of the three O-atoms is arbitrary. The *real* structure of carbonate has an electron distribution that is the mean of the three possible structures.



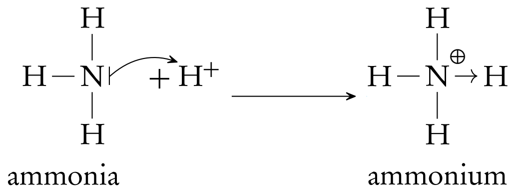
The resonance hybrid shows that the double bond is distributed between the three C=O bonds, *and* the square brackets with the charge shows that the formal charge is also distributed over the three O-atoms.

Coordinate covalent bond = dative bond

Dative Bond when an atom *donates a non-bonding pair* to another atom to form a covalent bond (instead of both of the atoms donating 1 electron to form a single covalent bond).

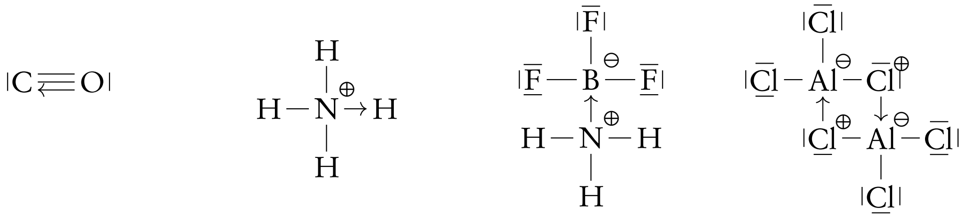
Dative bonding is particularly relevant for acids and bases since H^+ is an electron pair acceptor, as well as other Lewis acids. Ammonium forms after ammonia donates its non-bonding electron pair to an H^+-ion, shown in Figure 4.1.

Figure 4.1



Other (important) examples showing dative bonding are shown in Figure 4.2.

Figure 4.2



arbon monoxide
CO

ammonium
NH_4

NH_3BF_6

aluminium chloride
Al_2Cl_6

4.3.3 VSEPR: shapes of molecules and ions

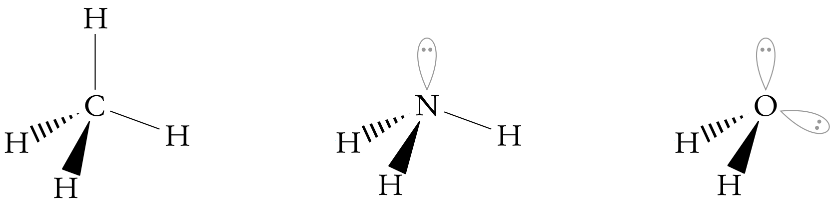
Electron domain every bonding or non-bonding pair surrounding an atom. Single, double and triple bonds *count as 1 electron domain*, because they are situated between two atoms in the same 'spatial domain'

VSEPR (Valence Shell Electron Pair Repulsion Theory) electron domains arrange around the central atom to be as far apart from each other as possible.

The shape of molecules and ions can be predicted by accounting the number of electron domains. The geometry of the central atom is a contraction of the number of electron domains, and the number of bonding vs. non-bonding electron pairs. *To determine the shape of a molecule you must always first draw the Lewis structure!*

Non-bonding electron domains have a stronger repulsion than bonding-electron domains. When a molecule has a non-bonding pair, it pushes the bonding pairs slightly closer together, resulting in decrease of 2.5° per non-bonding pair.

Figure 4.3



109.5° methane

107° ammonia

104.5° water

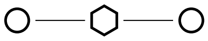
Methane, ammonia and water all have basic tetrahedral electron distribution, but each has an increasing number of non-bonding pair of electrons.

Electron domain geometry the 3d arrangement of atoms and non-bonding pairs that constitute a molecule

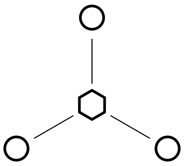
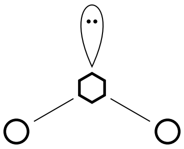
Molecular geometry the 3d arrangement of atoms that constitute a molecule

In the table below the central atom is draws as ⬡ and the surrounding atoms as ○. The lobe with two dots represents non-bonding pairs.

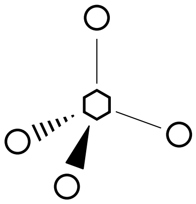
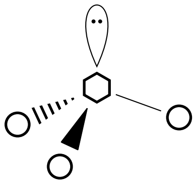
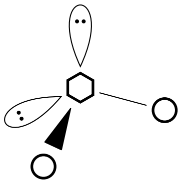
② electron domain

Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
2/4	0	linear	180°	

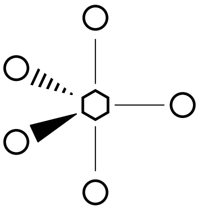
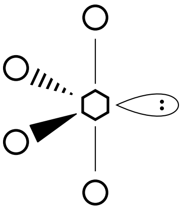
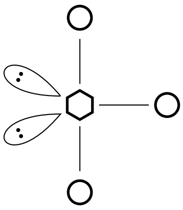
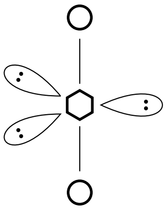
③ electron domain

Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
3/4	0	planar triangular	120°	
2/3	1	bent / v-shape	117.5°	

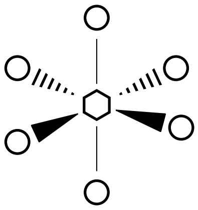
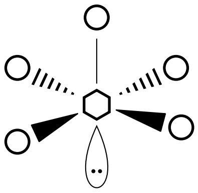
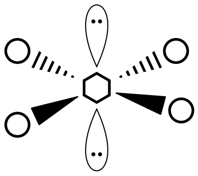
④ electron domain

Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
4	0	tetrahedral	109.5°	
3	1	trigonal pyramid	107°	
2	2	bent / v-shape	104.5°	

⑤ electron domain

Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
5	0	trigonal bipyramidal	90°/120°	
4	1	see-saw	90°/117.5°	
3	2	T-shape	90°	
2	3	linear	180°	

6 electron domain

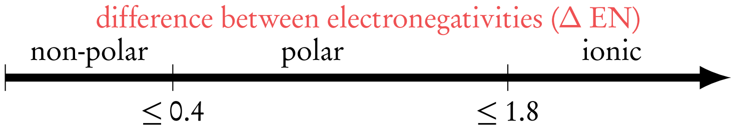
Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
6	0	octahedral	90°	
5	1	square pyramid	90°	
4	2	square planar	90°	

Polar bonds: from ionic to covalent bonding

See chapter 3 for the definition of electronegativity

Ionic bonds form when atoms *transfer* electrons, covalent bonds form when atoms *share* electrons. If only life was that simple! In reality, electrons of many covalent bonds are not shared equally: elements with a greater electronegativity (EN) have a greater pull on the shared electron pair resulting in a polar bond.

The element that has higher EN pulls e^- closer and so gains a partial negative charge ($\delta-$), leaving a slightly electron deficient atom with a partial positive charge (δ^+).



So the ΔEN between two elements determines whether the bond will be:

pure covalent: Δ EN ≤ 0.4 (approx. equal sharing)
polar covalent: $0.4 < \Delta$ EN ≤ 1.8 (unequal sharing)
ionic: Δ EN > 1.8(no longer 'sharing', e^- are transferred between atoms)

Whether a bond is covalent or polar covalent *inside* a molecule, directs the bonding *between* molecules – determining the material properties of molecular compounds.

4.4 Intermolecular forces

The physical properties of (simple) molecular compounds are determined by the bonding *between molecules*. There are three main types of bonding between molecules (= intermolecular bonding):

1. hydrogen bonding *(strongest & most polar)*
2. dipole-dipole bonding *(weaker & still polar)*
3. Londen dispersion forces *(weakest & non-polar)*

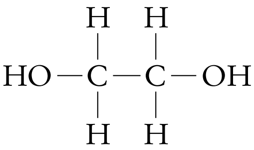
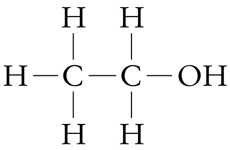
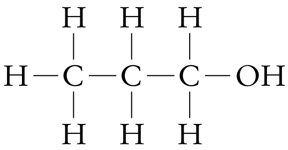
4.4.1 Hydrogen bonding

Hydrogen bonding a directional and medium strength bond between molecules that occurs when a molecule contains (—OH, —NH_x or HF).

When a H-atom is bound directly to a small very electronegative atom (O, N or F), the shared e^- pair is strongly pulled toward the electronegative atom. Since H has no inner shell electrons, the positive nucleus is exposed more than it would be for other elements. The larger unshielded charge allows the formation of hydrogen bonds.

The more H-bond forming groups a molecule has (relative to the size of the molecule), the more H-bonds can be formed and so the stronger the IMF, thus the higher MP/BP. This is illustrated in Table 4.2.

Table 4.2

	1,2-ethanediol	ethanol	1-propanol
Structure	 $HO-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$	 $H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$
BP	197.3 °C	78 °C	97 °C
MP	−12.9 °C	−114 °C	−126 °C

4.4.2 Dipole-dipole forces

Dipole molecule a molecule with asymmetrically distributed partial negative and positive charge

- Presence of a polar bond: Δ EN > 0.4
- Asymmetric distribution of $\delta+$ and $\delta+$

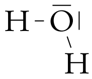
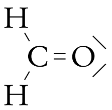
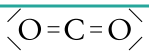
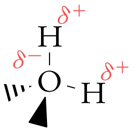
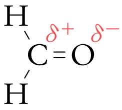
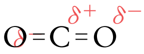
Dipole-dipole bond electrostatic attraction between the partial charges of two dipole molecules

$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \qquad \overset{\delta+}{H}-\overset{\delta-}{Cl}$$

Ion-dipole bond electrostatic attraction between an ion and the partial charge of a dipole molecule

$$\overset{\delta+}{H}-\overset{\delta-}{Cl} \qquad Na^+ \qquad \overset{\delta-}{Cl}-\overset{\delta+}{H}$$

Identifying dipole molecules

		H_2O	H_2CO	CO_2
1.	Draw the Lewis structure			
2.	Polar bonds? $(0.4 < \Delta EN < 1.8)$	OH: $3.5 - 2.1 = 1.4$	CH: $2.5 - 2.1 = 0.4$ CO: $3.5 - 2.5 = 1.0$	CO: $3.5 - 2.5 = 1.0$
3.	Draw the 3D molecule			
4.	Geometric charge distribution?	No: dipole molecule	No: dipole molecule	Yes: not a dipole molecule

Bond strength

Electrostatic attraction increases as the charge difference increases. So:
- ion-dipole > dipole-dipole > dipole-induced dipole
- polar bonds with larger ΔEN > less polar bonds with smaller ΔEN

4.4.3 London (dispersion) forces

Never use the term 'van der Waals forces', which is a collective term for several forces, because the IB is very strict about naming the precice type of bonding that occurs.

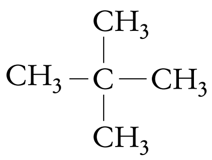
London Dispersion (LD) forces electrons oscillate in all molecules, causing a temporary instantaneous dipole. This in turn can induce a temporary instantaneous dipole in a neighbouring molecule, resulting in a weak electrostatic attraction between the molecules

Bond strength

Heavier molecules tend to have more electrons, so it is common to say that the strength of the London dispersion forces increases with molecular mass.

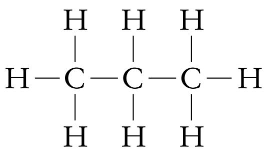
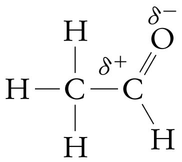
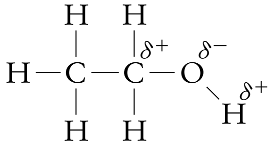
The LD forces increase as the polarisability of molecules increases:
- as the number of electrons increases = the mass of a molecule increases.
- as the surface area of a molecule increases. Branched molecules have a smaller surface area, are less polerizable, so they experience smaller LD forces.

	mass	BP
F_2	38 u	−188 °C
Cl_2	71 u	−34 °C
Br_2	160 u	58 °C
I_2	254 u	183 °C

	mass	BP
$CH_3-CH_2-CH_2-CH_2-CH_3$	72 u	36 °C
 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$	72 u	10 °C

4.5 Properties of molecular compounds

Note that the properties of simple molecular compounds are very different from giant covalent compounds. The properties of (simple) molecular compounds depends on the type of attractive forces *between* the molecules, in order of decreasing strength: hydrogen bonding > dipole-dipole > London dispersion forces.

	Propane	Ethanal	Ethanol
molar mass	$44\,\mathrm{g\,mol^{-1}}$	$44\,\mathrm{g\,mol^{-1}}$	$46\,\mathrm{g\,mol^{-1}}$
structure			
boiling point	−42.2 °C	20.8 °C	78.5 °C
bonding type	London dispersion	dipole-dipole London dispersion	hydrogen bonding dipole-dipole London dispersion
polarity	non-polar	polar	polar

Melting-/boiling point

Comparing molecules of approximately the same molar mass (constant London dispersion forces); molecules that form hydrogen bonds will have highest MP/BP, then dipole molecules, then molecules that only experience LD forces.

Note: the weaker the intermolecular forces, the lower the MP/BP *and* the more volatile the substance.

Solubility

Like tends to dissolve like: so polar compounds dissolve well in polar solvents (e.g., water), and nonpolar compounds in nonpolar solvents (e.g., oil, hexane).

Tip: when asked what type of bonding is present *all* types must be given. So do not forget about LD-forces, as they are always present.

Conduction

The requirements for conduction are that there are *charged particles* which *can move*. Molecular compounds are never charged, and so can never conduct electricity. (But ions that are dissolved in tap water can conduct electricity)

Malleability

Whether molecular compounds are malleable depends on the type, directionality and strength of intermolecular forces. Generally speaking, hydrogen bonds and giant covalent bonds are highly directional, so solids wherein these play a key-role are not malleable. Nevertheless, a huge range between brittle (e.g., glass) and malleable (e.g., clay) exists.

4.5.1 Giant covalent structures

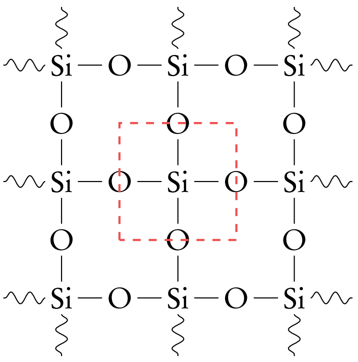
Giant covalent structures all the atoms are bonded by covalent bonds in a continuous network extending throughout the material

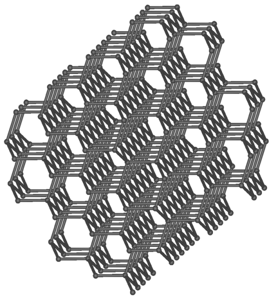
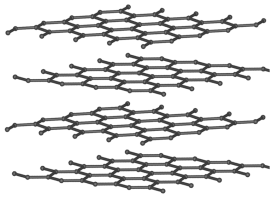
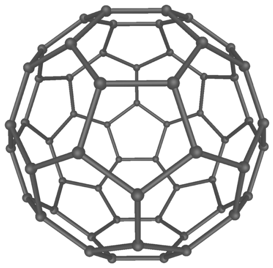
Allotropes occur when an element can exist in different crystalline forms.

In a network solid there are no individual molecules, and therefore no *inter*molecular forces. The entire solid may be considered one big macromolecule. The chemical formula is the simplest ratios of the component atoms (empirical formula).

Examples of giant covalent structures are diamond and graphite (discussed below), and SiO_2 which is the chemical formula for silica and quartz. Since every O-atom is shared between two Si-atoms, we can say that every Si-atom is bonded to four halves of an O-atom; in other words that for every one Si-atom there will be two O-atoms.

Structure of SiO_2



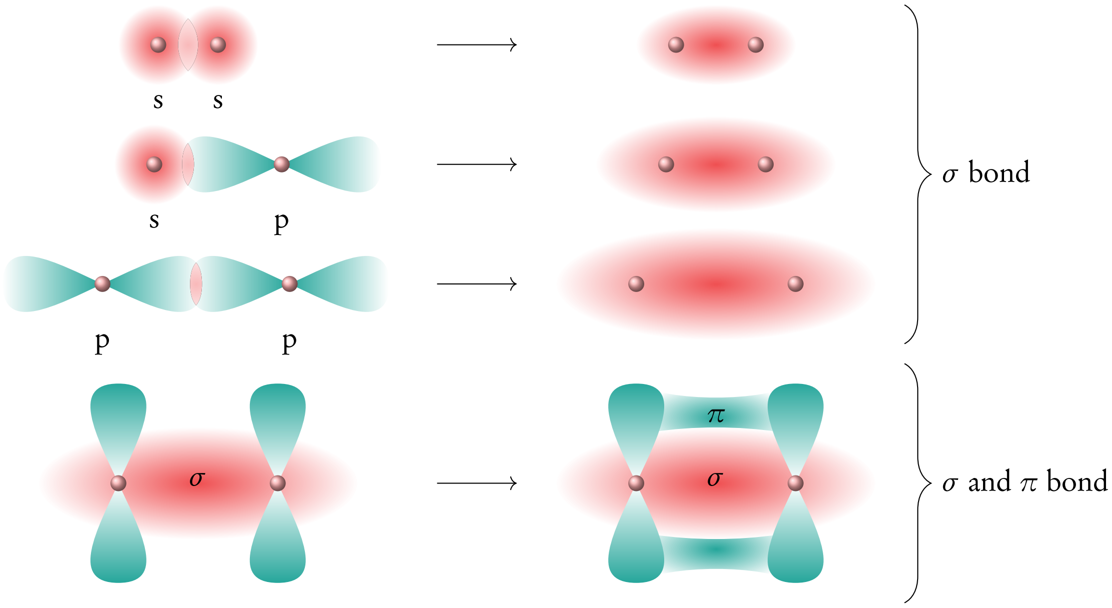
allotropes of C	Diamond	Graphite	Fullerene
			
hybridisation	sp^3	sp^2	sp^2
shape	tetrahedral	trigonal planar	trigonal planar
macrostructure	network	stacked flat layers of hexagonal C lattices	hexagonal C lattice folded in on itself
bond angles	109.5°	120°	$< 120°$
bonds	single bonds	1× double bond	1× double bond
conduction	no, e^- cannot move	yes, delocalised e^- can move between layers	yes, delocalised e^- can move over surface

4.6 Molecular orbitals

Atomic orbitals fuse to form new 'molecular orbitals':

σ bond is formed when two atomic orbitals overlap head-on (along a line drawn through the two atoms). Single or first bond between atoms.

π bond is formed when two atomic orbitals overlap sideways (forming two regions of electron density on opposite sides of the σ bond). Second/third bond between atoms.



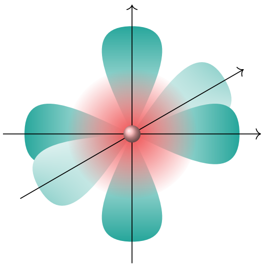
4.7 Hybridization: mixing atomic orbitals

Hybridization the mixing of atomic orbitals of different energy to obtain homogeneous orbitals of the same (degenerate) energy

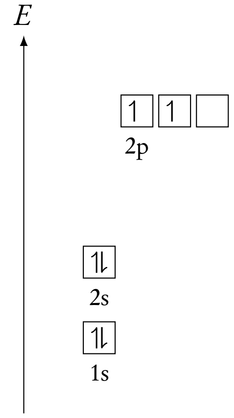
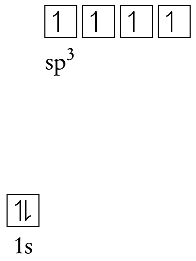
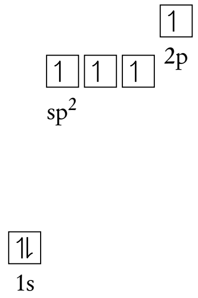
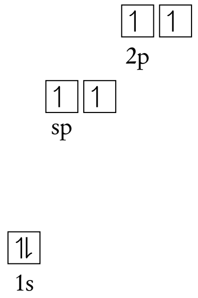
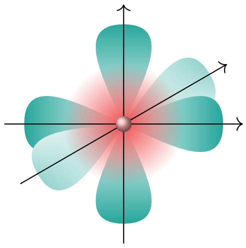
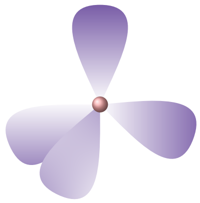
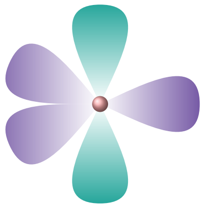
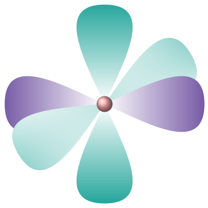
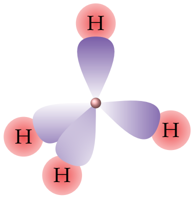
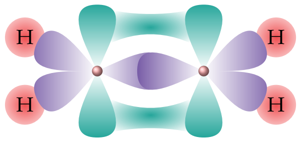
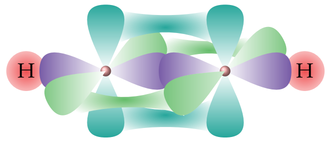
The atomic s and p orbitals mix to form new hybrid orbitals, to form covalent bonds with other atoms. The shape and energy level of the new orbitals are a mix of the constituent s and p atomic orbitals.

In the image on the side, the atomic 2s and 2p subshells of C are not hybridized. From it we cannot deduce why carbon has bond angles of 109.5°. In order to understand the bond geometry of C we have to mix atomic orbitals:

- mix one s-orbital with three p-orbitals to get four degenerate sp^3 orbitals.
- mix one s-orbital with two p-orbitals to get three degenerate sp^2 orbitals and one p-orbital.
- mix one s-orbital with two p-orbitals to get two degenerate sp orbitals and two degenerate p-orbitals.



non-hybridized C

Unhybridised	sp^3 hybridised	sp^2 hybridised	sp hybridised
			
			
Bond type	only single	1× double	1× triple or 2× double
Example			
Basic geometry **Bond angles**	tetrahedral 109.5°	planar triangular 120°	linear 180°

4.8 Ozone and oxygen

Ozone absorbs UV light, protecting us from its ionizing effects (UV light posseses sufficient energy to ionize certain molecules, which causes skin cancer when ionizing DNA of skin cells). When the atmosphere contains less ozone, less UV light is absorbed.

When the formation of ozone equals the depletion of ozone, there is no net change (= steady state). Human-made pollutants such as CFCs and nitrogen oxides have disrupted the steady state.

Formation of ozone

Photodissociation process whereby chemical bonds absorb enough light energy to break them

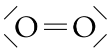
Ozone is continuously produced naturally in the stratosphere by the photodissociation of oxygen. The strong O=O bond requires high energy UV light from the sun to break the bond, forming O atoms. Since O atoms do not have an octet they are very reactive, and will react with another O_2 molecule to form ozone O_3.

many IB study guides incorrectly state that radicals are formed here but this is not true!

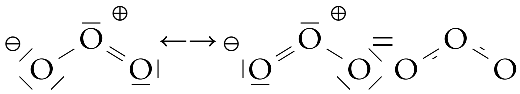
$$\mathrm{O{=}O(g)} \xrightarrow{\text{high energy UV}} 2\,\mathrm{O(g)}$$
$$\mathrm{O(g)} + \mathrm{O_2(g)} \longrightarrow \mathrm{O_3(g)}$$

Ozone protection mechanism

As discussed in section 4.3 covalent bonding; double bonds are stronger than single bonds.



oxygen



ozone

The O=O double bond in O_2 is stronger than the O=O bond in O_3 (which is in strength somewhere between a single and a double bond). To break a bond in O_3, less energy is required than to break the bond in O_2. So while oxygen can absorb light with wavelengths < 240 nm, ozone absorbs light with wavelengths < 390 nm, thus offering protection against UV light with wavelengths between 240 nm to 390 nm.

Remember:
the bond strengths & lengths in ozone are equal due to the resonance effect.

When O_3 absorbs light, one ozone bond breaks forming O_2 and an O atom:

$$O_3(g) \xrightarrow{\text{medium energy UV}} O(g) + O_2(g)$$

Ironically, when ozone protects us it gets destroyed in the process. Or does it? In fact, ozone is formed again if the O atom (which is reactive due to it not having a stable octet) collides with an O_2 molecule – which probability is much larger than two O atoms colliding to form O_2.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

The ozone is regenerated, ready to absorb another high energy photon!

4.8.1 Depletion of ozone

Radical a highly reactive molecule that contains an unpaired electron

Radicals form due to the homolytic fission of a covalent bond, leaving the two fragements both with an unpaired electron. The radical can wreak all kinds of havoc during various propagation steps, whereby a radical reacts with a non-radical forming a non-radical and a radical. Finally, when to radicals collide these can form a pair again, terminating both radicals.

When CFC molecules such Freon-12 (CCl_2F_2) enter the stratosphere radical initiation occurs by absorbing UV light. For many propagation cycles the radicals will react with O_3.

It is estimated that a single CFC molecule on average breaks down 10^5 O_3 molecules.

Simaraly nitrogen oxides decompose ozone by a (different) radical reaction mechanism. Although the mechanism is too complex, the overall reaction can be written as (with NO_x as a catalyst for ozone breakdown):

$$2O_3 \longrightarrow 3O_2$$

ENERGETICS

5

Temperature T a measure of the average kinetic energy of particles in a substance
(= independent of the amount of substance)

Heat Q the amount of thermal energy in a given amount of substance
(= proportional to the amount of substance)

Heat is a form of energy exchange, its direction depends on the difference in temperature. Heat flows from a warmer to a cooler substance.

Enthalpy H the amount of chemical potential energy contained in one mol of a substance, stored in its chemical bonds.

Read “enthalpy” as “chemical energy”

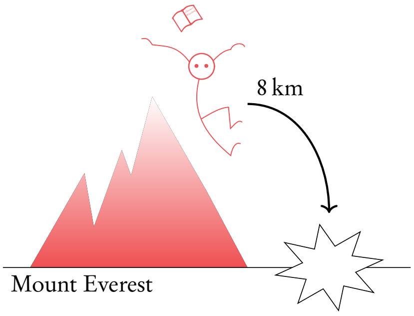
Higher enthalpy: substance has weaker bonds, can release more heat.

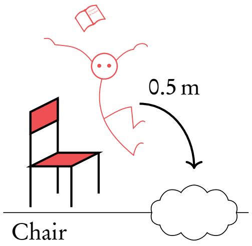
Lower enthalpy: substance has stronger bonds, can release less heat.

The absolute value of enthalpy cannot be measured, so we measure the *enthalpy change* (ΔH) between products and reactants in $\mathrm{kJ\,mol^{-1}}$.

Enthalpy: chemical potential energy

Chemical energy is a form of potential energy, like gravitational potential energy. Falling from a height of 8 km is deadlier than falling from 1 m, since a lot of gravitational potential energy is converted into kinetic energy.





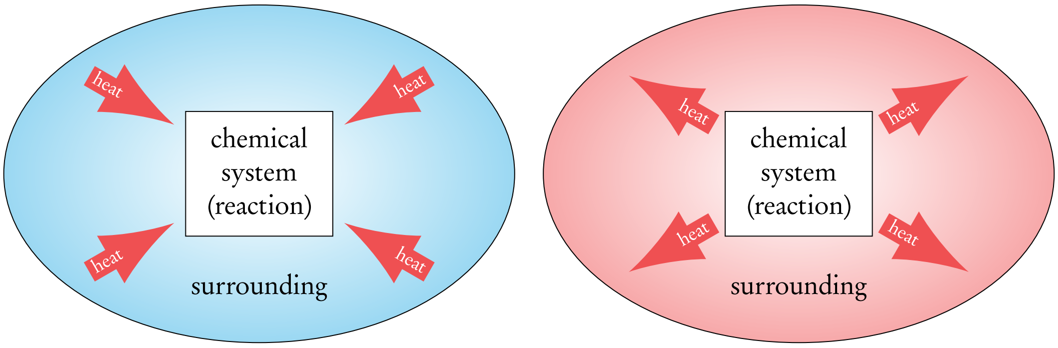
Although the stickman on top of the mountain has a huge amount of potential energy, this has no effect on the amount of his kinetic energy at the top. The kinetic energy (of his fall) depends on the *height difference*.

The amount of heat released or absorbed by a chemical reaction depends on the *height difference* between the initial and final enthalpy. Importantly, the average kinetic energy (temperature) of a system does not depend on the amount of enthalpy!

Chemical system and the surrounding

It is important to make the distinction between a *chemical system* and its *surroundings*. The sytem consists of a chemical reaction: breaking chemical bonds requires energy (thus cooling the surrounding), while forming chemical bonds releases energy (thus heating the surrounding). Energy is exchanged between the system and its surrounding.

In other words, *enthalpy* (H) can be converted into *heat* (Q), and vice versa. The heat increase is equal to the enthalpy decrease.



heat (Q) is converted to enthalpy (H)
the surrounding cools down
endothermic

enthalpy (H) is converted to heat (Q)
the surrounding heats up
exothermic

Measuring enthalpy: calorimetry

To accelerate a train requires much more energy than a pedestrian. Similarly, different substances require different amounts of energy to increase their temperature by 1 K. To increase the temperature of 1 kg of water by 1 K requires 4.18 kJ, while iron would require ten times less energy (0.412 kJ).

Note that a *temperature change* of 1 K corresponds to a *change* of 1 °C

Specific heat capacity (c) the amount of heat in kJ (or J) to increase the temperature of 1 kg (or 1 g) of substance by 1 K.

Note that the temperature can *always* be input as either K or °C in *this* expression, but that mass in kg yields kJ, while g will yield J.

The change in the amount of heat is given by:

$$\Delta Q = cm\Delta T$$

ΔQ = heat change [kJ] or [J]
c = specific heat cap. [kJ kg^{-1} K^{-1}] or [J g^{-1} K^{-1}]
m = mass [kg] or [g]
ΔT = temperature change [K] or [°C]

In order to measure the enthalpy change of a chemical reaction, we can measure the equal but opposite heat change of the surroundings. We assume that all the heat released or used by a chemical reaction is used to change the temperature of the surroundings (no heat loss). Furthermore, enthalpy is defined per mol reactant resulting in the following expression:

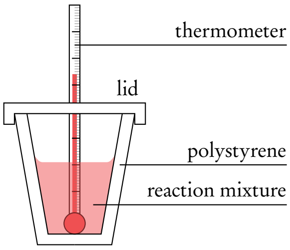
$$\Delta H = -\frac{\Delta Q_{\text{surrounding}}}{n_{\text{system}}}$$

ΔH = enthalpy change [kJ mol^{-1}]
$\Delta Q_{\text{surrounding}}$ = heat change [kJ]
n_{system} = mole amount [mol]

Note: convert heat to kJ before using this expression, since the databook and the exam will always use kJ mol^{-1} as units for the enthalpy change.

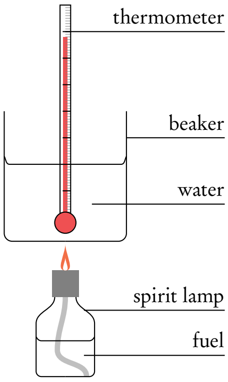
Calorimetry is a technique to measure the increase or decrease in heat by measuring the temperature change of the surrounding, typically that of water ($c = 4.18\,\text{J g}^{-1}\,\text{K}$). Under the assumption that no heat is lost, the enthalpy change of a chemical reaction can be calculated from its effect on the temperature of its surrounding.

Calorimetry: aqueous reaction



The temperature change caused by a chemical reaction in aqueous solution is measured. Assume that all heat is transferred to the water.

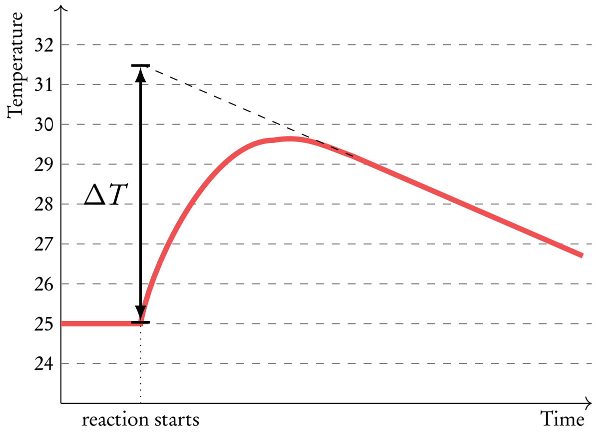
Calorimetry: combustion



Assume that all the heat that is released by the combustion reaction is absorbed by the water.

Example.

Determine ΔT from a graph



Extrapolate the graph *up to the point when the reaction starts*. This point represents the maximum temperature if the reaction had been instantaneous (no heat loss).

$$\begin{aligned}\Delta T &= T_{\text{end}} - T_{\text{start}}\\ &= 31.5\,^{\circ}\text{C} - 25.0\,^{\circ}\text{C}\\ &= 6.5\,^{\circ}\text{C}\end{aligned}$$

Calculate the enthalpy change ΔH, when the temperature change ΔT of the surrounding is given

Calculate the enthalpy of combustion for P_4 from the given data:

Mass of water	g	150.00
Initial temperature	°C	25.0
Final temperature	°C	31.5
Mass of phosphorus burned	g	0.0500

1. Calculate number of moles of *the limiting reactant*

$$n(\mathrm{P_4}) = \frac{m(\mathrm{P_4})}{M(\mathrm{P_4})} = \frac{0.0500\,\mathrm{g}}{4 \times 30.97\,\mathrm{g\,mol^{-1}}}$$
$$= 4.04 \times 10^{-4}\,\mathrm{mol}$$

2. Calculate heat change (ΔQ) of *the surrounding*

The temperature of the water changes:

$$\Delta Q = cm\Delta T$$
$$= 4.18 \cdot 150.00 \cdot (31.5 - 25.0)$$
$$= 4.08 \times 10^3\,\mathrm{J} = 4.08\,\mathrm{kJ}$$

3. Use these two values to calculate $\Delta\mathrm{H}$. Convert to kJ first, and invert the sign

$$\Delta H = -\frac{\Delta Q}{n(\mathrm{P_4})} = -\frac{4.08\,\mathrm{kJ}}{4.04 \times 10^{-4}\,\mathrm{mol}}$$
$$= -1.01 \times 10^4\,\mathrm{kJ\,mol^{-1}}$$

The reaction is exothermic since ΔH = negative, which is logical because all combustion reactions are exothermic

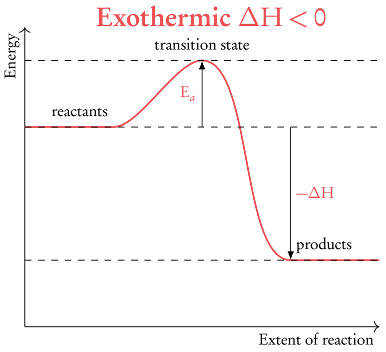
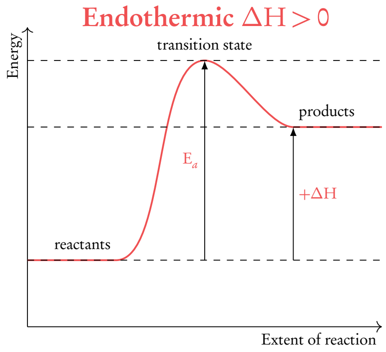
5.2 Energy diagrams

A chemical reaction can use heat from the surrounding $(T\downarrow)$ to break bonds in the system (increasing enthalpy). Or the opposite, release heat to the surrounding $(T\uparrow)$ when bonds are formed (decreasing enthalpy).

In typical chemical reactions both processes occur: bonds are broken and new bonds are formed. And like your bank account, at the end of the month your balance will have increased or decreased by some net amount. When the net amount of enthalpy decreases (heat increases) a reaction is said to be exothermic, and when the net amount of enthalpy increases (heat decreases) a reaction is endothermic.

Exothermic reaction heat is released by reaction to the surroundings $(T\uparrow)$, the enthalpy H *decreases* or $\Delta H < 0$.

Endothermic reaction heat is used by reaction from the surroundings $(T\downarrow)$, the enthalpy H *increases* or $\Delta H > 0$.

Diagrams		
Sign of ΔH	− (negative)	+ (positive)
Enthalpy ΔH	decreases	increases
Heat ΔQ	increases	decreases
Temperature T	increases	decreases
Bond strength	bonds in products are stronger than the bonds in the reactants	bonds in products are weaker than the bonds in the reactants
Typical examples	bond formation, combustion, acid/base neutralisation, ...	bond breaking, ionization (!), ...

5.3 Hess's law

Hess's law the enthalpy change (ΔH) of a reaction depends only on the difference between the enthalpy of the products and reactants, it is independant of the reaction pathway.

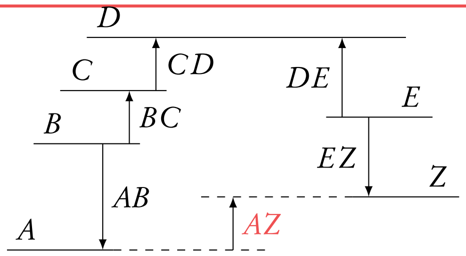


Figure 5.1

The elevation difference AZ equals the sum of all the individual distances from A to Z. Starting at A, let's walk over the diagram to Z via the levels B, C, D, and E.

$$AZ = -AB + BC + CD - DE + EZ$$

So whenever an arrow is in the wrong direction simply change the sign to reverse the arrow in the correct direction.

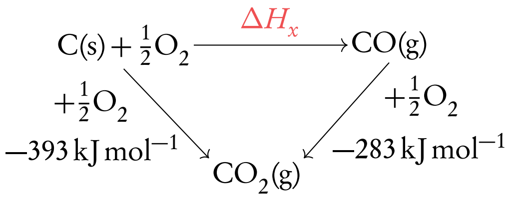


Figure 5.2

The diagram above in Figure 5.2 shows a typical exam question. To calculate ΔH_x, start on the reactant side (left) and take the long route (via CO_2) in the direction of the product (right). Flip the direction of the arrows by changing the sign of the values.

$$\begin{aligned}\Delta H_x &= -394\,\text{kJ}\,\text{mol}^{-1} + 283\,\text{kJ}\,\text{mol}^{-1}\\ &= -111\,\text{kJ}\,\text{mol}^{-1}\end{aligned}$$

Another typical application of Hess's law on the exam is when multiple component reaction equations and their corresponding ΔH values are given, and you have to calculate the enthalpy change of a reaction that is a composite of the component reactions.

Enthalpy change from component reactions

Consider the following equations:

$$2\,\text{Fe(s)} + 1\tfrac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{Fe}_2\text{O}_3\text{(s)} \qquad \Delta H = x$$

$$\text{CO(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \qquad \Delta H = y$$

What is the enthalpy change of the overall reaction below?

$$\text{Fe}_2\text{O}_3\text{(s)} + 3\text{CO(g)} \longrightarrow 3\text{CO}_2\text{(g)} + 2\text{Fe(s)}$$

1.	Identify the unique compounds in the given reaction equations	In the first reaction Fe and Fe_2O_3, and in the second CO and CO_2.
2.	Are the unique compounds on the same side as in the overall reaction?	Fe and Fe_2O_3 are on the opposite sides in the overall reaction. So we invert: $\text{Fe}_2\text{O}_3\text{(s)} \longrightarrow 2\,\text{Fe(s)} + 1\tfrac{1}{2}\text{O}_2\text{(g)} \quad \Delta H = -x$
3.	Do the unique compounds have the correct reaction coefficients?	CO and CO_2 have coefficients 3 in the overall reaction. Multiply by three: $3\text{CO(g)} + 1\tfrac{1}{2}\text{O}_2\text{(g)} \longrightarrow 3\text{CO}_2\text{(g)} \quad \Delta H = 3y$
4.	Add the ΔH values to get the ΔH value of the overall reaction	$\Delta H = -x + 3y$

Enthalpy change from component reactions

$$\text{C} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \qquad \Delta H = -394\,\text{kJ}$$

$$\text{CO(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \qquad \Delta H = -283\,\text{kJ}$$

Calculate the enthalpy change using the given data for: $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO(g)}$

1.	Identify the unique compounds in the component equations	C in the first, CO in the second reaction.
2.	Are the unique compounds on the same side as in the overall reaction?	C is on the correct side, CO on the wrong side so invert the equation: $\text{CO}_2\text{(g)} \longrightarrow \text{CO(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \quad \Delta H = 283\,\text{kJ}$
3.	Do the unique compounds have the correct reaction coefficients?	Yes they already do, so do nothing
4.	Add the ΔH values to get the ΔH value of the overall reaction	$\Delta H = -394\,\text{kJ} + 283\,\text{kJ} = -111\,\text{kJ}$

5.3.1 Standard enthalpy of formation

Standard state (symbol $= ^{\ominus}$) is the most stable state of an element or compound under the standard conditions (pressure 100 kPa, temperature 298 K)

(Standard) enthalpy of formation $H_f^{\ominus}$ the enthalpy change when *one mole* of a substance is formed *from its elements in their standard states* (at *standard conditions*).

$H_f^{\ominus} = 0$ for: elements in their standard state (e.g. $C_{graphite}(s)$, $Fe(s)$, $O_2(g)$, …)

$$\begin{array}{ll} H_f^{\ominus} \text{ of } CH_4 \text{ is:} & C_{graphite}(s) + 2H_2(g) \longrightarrow CH_4(g) \\ H_f^{\ominus} \text{ of } H_2O \text{ is:} & H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \end{array}$$

Enthalpy of formation is defined identically, just not specifically from their *standard states*

Figure 5.3 shows the standard enthalpy of formation for NO_2 on the left, and N_2O_2 in the middle. On the right we see the composite energy diagram for the reaction $2NO_2 \longrightarrow N_2O_4$.

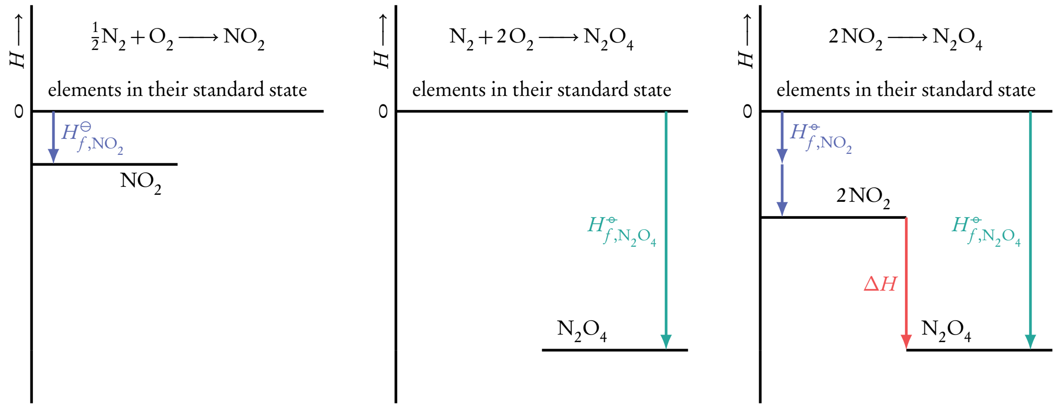


Figure 5.3

Using Hess's law (invert reactant side): $\Delta H = \sum H^{\ominus}_{f,products} - \sum H^{\ominus}_{f,reactants}$

5.3.2 Bond enthalpy

Bond breaking is always endothermic

(Average) bond enthalpy H_b is the amount of energy required to break *one mole* of the *same type of bond, in the gasous state*, (averaged over a variety of *similar compounds.*)

All compounds *must* be in the gaseous state

$H_b = 0$ for: free gaseous atoms (e.g. H(g), C(g), Fe(g), O(g), ...)

$CH_4 \longrightarrow CH_3 + H$ requires $435\,\mathrm{kJ\,mol^{-1}}$, $CH_3 \longrightarrow CH_2 + H$ requires $444\,\mathrm{kJ\,mol^{-1}}$. So instead we take 1/the number of bonds in the molecule.

H_b of the C—H bond in CH_4 is: $\frac{1}{4}CH_4(g) \longrightarrow \frac{1}{4}C(g) + H(g)$

H_b of the O—H bond in H_2O is: $\frac{1}{2}H_2O(g) \longrightarrow H(g) + \frac{1}{2}O(g)$

Figure 5.4 shows the bond enthalpy of the reactants ($H_2 + F_2$) on the left, and the product enthalpy (HF) is shown in the middle. On the right we see the composite energy diagram for the reaction $H_2 + F_2 \longrightarrow HF$.

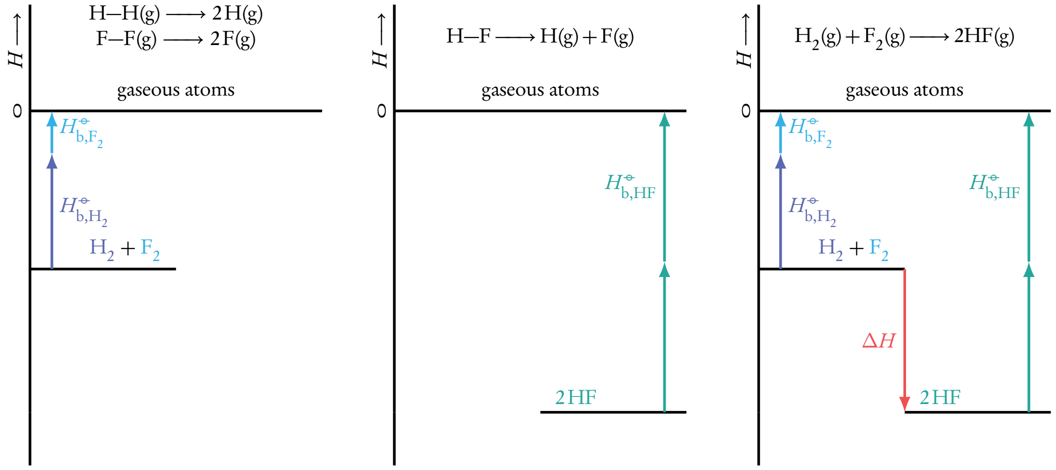


Figure 5.4

Using Hess's law (invert product side): $\Delta H = \sum H_{b,\text{reactants}} - \sum H_{b,\text{products}}$

Limitations of average bond enthalpies

- Bond enthalpies require that all compounds are in the gaseous state.
- Since average bond enthalpies are obtained by considering a number of similar compounds containing the type of bond in question, the bond energy in any particular compound may deviate.

5.3.3 Enthalpy of combustion

(Standard) enthalpy of combustion $H_c^\ominus$ is the amount of energy released for the *complete combustion* of *one mole* of substance *in its standard state* and in *excess oxygen* (at *standard conditions*).

$H_c^\ominus = 0$ for: complete combustion products under standard conditions (e.g. $CO_2(g)$, $H_2O(l)$, …)

$H_c^\ominus$ of CH_4 is: $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
$H_c^\ominus$ of $C_6H_{12}O_6$ is: $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

Combustion reactions are exothermic

Figure 5.5 shows the combustion enthalpies of the reactants ($C_2H_4 + H_2$) on the left, and the product (C_2H_6) is shown in the middle. On the right we see the composite energy diagram for the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$.

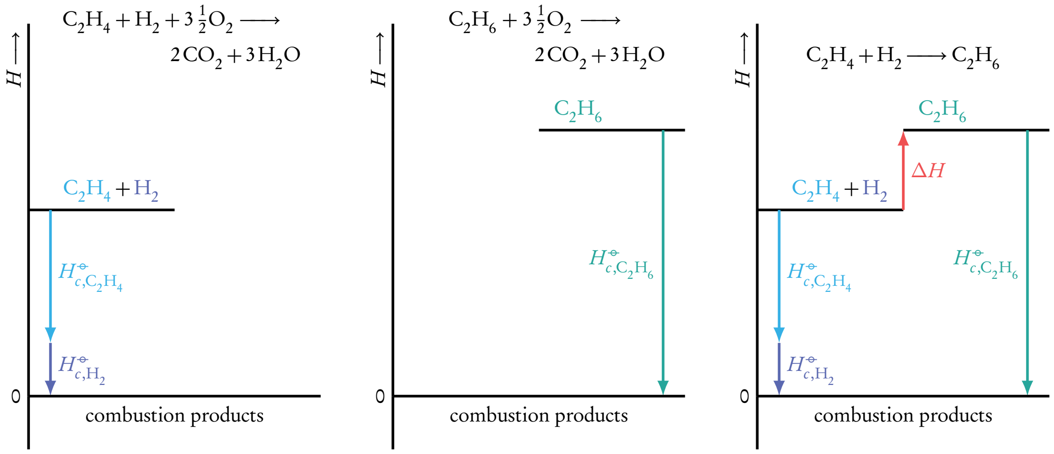


Figure 5.5

Using Hess's law (invert product side): $\Delta H = \sum H^\ominus_{\text{c,reactants}} - \sum H^\ominus_{\text{c,products}}$

5.4 Energy calculations

Enthalpy calculations can be done by using either the enthalpy of formation, bond enthalpy ***or*** the enthalpy of combustion. Since enthalpy values are relative to $H = 0$, and this is different in all three cases, the three types of values cannot be used in *the same* calculation.

	Formation	Bond	Combustion
$H = 0$	elements at SATP	gaseous atoms	combustion products at SATP
Definition	forming product	breaking reactant bonds	burning reactant
$\Delta H =$	$\sum H^{\ominus}_{f,prod} - \sum H^{\ominus}_{f,react}$	$\sum H^{\ominus}_{b,react} - \sum H^{\ominus}_{b,prod}$	$\sum H^{\ominus}_{c,react} - \sum H^{\ominus}_{c,prod}$

When calculating $\sum H$ remember to multiply the enthalpy values with the reaction coefficients
× number of molecules

Calculate reaction enthalpy (formation)

Calculate the reaction enthalpy using the standard enthalpies of formation for:

$$C_2H_6(g) + Cl_2(g) \longrightarrow C_2H_5Cl(g) + HCl(g)$$

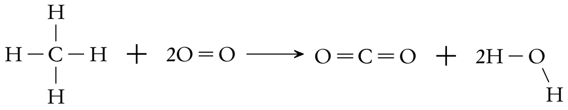
1.	Write the reaction equation	$C_2H_6(g) + Cl_2(g) \longrightarrow C_2H_5Cl(g) + HCl(g)$
2.	Find the enthalpy values (DB. 11-13) *remember:* when is $H = 0$?	$-84 \quad 0 \quad -137 \quad -92.3$
3.	Calculate $\sum H_{reactant}$ and $\sum H_{product}$ *seperately*	$\sum H_{reactant} = 1\times -84 + 1\times 0$ $= -84\,kJ$ $\sum H_{product} = 1\times -137 + 1\times -92.3$ $= -229\,kJ$
4.	Use the correct formula for $\Delta H =$ formation: $\sum H_{f,prod} - \sum H_{f,react}$ bond/combustion: $\sum H_{react} - \sum H_{prod}$	$\Delta H = \sum H_{f,product} - \sum H_{f,reactant}$ $= -229 - -84\,kJ\,mol^{-1}$ $= -145\,kJ\,mol^{-1}$

Calculate reaction enthalpy (bond)

Calculate the reaction enthalpy using the bond enthalpies for:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

1. Write the reaction equation *in structural formulas*



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}{-}H} + 2\mathrm{O{=}O} \longrightarrow \mathrm{O{=}C{=}O} + 2\mathrm{H{-}O{-}H}$$

2. Find the enthalpy values (DB. 11-13)

$C-H$: 414 $C=O$: 804

$O=O$: 498 $O-H$: 463

3. Calculate $\sum H_{\text{reactant}}$ and $\sum H_{\text{product}}$ *seperately*

$$\sum H_{\text{reactant}} = 4\times 414 + 2\times 498$$
$$= 2652\,\text{kJ}$$
$$\sum H_{\text{product}} = 2\times 804 + 2\times 2\times 463$$
$$= 3460\,\text{kJ}$$

× bonds per molecule
× number of molecules

4. Use the correct formula for $\Delta H =$

$$\Delta H = \sum H_{\text{b,reactant}} - \sum H_{\text{b,product}}$$
$$= 2652 - 3460\,\text{kJ mol}^{-1}$$
$$= -808\,\text{kJ mol}^{-1}$$

Calculate reaction enthalpy (combustion)

Calculate the reaction enthalpy using the standard enthalpies of combustion for:

$$CH_3COOH(l) \longrightarrow CH_4(g) + CO_2(g)$$

1. Write the reaction equation

$$CH_3COOH(l) \longrightarrow CH_4(g) + CO_2(g)$$

2. Find the enthalpy values (DB. 11-13)
remember: when is $H = 0$?

-874 -891 0

CO_2 is a product of complete combustion, so $H_c^{\ominus} = 0$

3. Calculate $\sum H_{\text{reactant}}$ and $\sum H_{\text{product}}$ *seperately*

$$\sum H_{\text{reactant}} = 1\times -874$$
$$= -874\,\text{kJ}$$
$$\sum H_{\text{product}} = 1\times -891 + 1\times 0$$
$$= -891\,\text{kJ}$$

× number of molecules

4. Use the correct formula for $\Delta H =$
formation: $\sum H_{\text{f,prod}} - \sum H_{\text{f,react}}$
bond/combustion: $\sum H_{\text{react}} - \sum H_{\text{prod}}$

$$\Delta H = \sum H_{\text{c,reactant}} - \sum H_{\text{c,product}}$$
$$= -874 - -891\,\text{kJ mol}^{-1}$$
$$= 17\,\text{kJ mol}^{-1}$$

5.5 Energy cycles

Energy cycles (such as the Born-Haber cycle) are another application of Hess's law, meaning as much as: "start at the reactant enthalpy level and add all the values while moving toward the product energy level". See Figure 5.1 on 67.

Enthalpy of atomization H_{AT} the enthalpy change when *one mole* of *gaseous atoms* are formed from the *elements in their standard states*.

$$C_{graphite}(s) \longrightarrow C(g)$$
$$\tfrac{1}{2}Cl_2(g) \longrightarrow Cl(g)$$

NB: for *gaseous* diatomic elements such as O_2, Cl_2, …: $H^{\ominus}_{AT} = \frac{1}{2}H^{\ominus}_{b}$

Breaking bonds in the element, and vaporisation/sublimation both require energy, so endothermic.

Ionization enthalpy H_{IE} the enthalpy change when *one mole* of *gaseous atoms* each lose one electron to form *one mole* of *gaseous* 1+ *ions*.

$$H_{1^{st}IE}: \quad Mg(g) \longrightarrow Mg^{+}(g) + e^{-}$$
$$H_{2^{nd}IE}: \quad Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-}$$

The second ionisation ethalpy is actually defined as the enthalpy change when *one mole* of *gaseous* 1+ *ions* each lose one electron to form *one mole* of *gaseous* 2+ *ions*.

Electron affinity enthalpy H_{EA} the enthalpy change when *one mole* of *gaseous atoms* acquire one electron forming *one mole* of *gaseous* 1— *ions*.

$$H_{1^{st}EA}: \quad O(g) + e^{-} \longrightarrow O^{-}(g)$$
$$H_{2^{nd}EA}: \quad O^{-}(g) + e^{-} \longrightarrow O^{2-}(g)$$

Standard lattice enthalpy $H^{\ominus}_{lattice}$ the enthalpy change when *one mole of a solid ionic compound* is separated into *gaseous ions* at *standard conditions*

$$NaCl(s) \longrightarrow Na^{+}(g) + Cl^{-}(g)$$
$$Ba_2(PO_4)_3(s) \longrightarrow 2Ba^{2+}(g) + 3PO_4{}^{3-}(g)$$

Ionic bonds are fairly strong, so separating an ionic solid into its constituent (gaseous) ions *requires a lot of energy*. So endothermic.

NB: lattice enthalpy is sometimes defined as the ionic solid *formed* from its gaseous ions. This inverts the sign of the enthalpy, but not its magnitude.

Magnitude of lattice enthalpy: depends on the ionic bond strength. The ionic bond strength increases when:

- the ions are smaller (up a group)
- the ions have larger charge

Enthalpy of hydration $H^{\ominus}_{\text{hydration}}$ the enthalpy change when *one mole* of *gaseous ions* dissolve in water, forming an infinitely dilute solution.

$$\mathrm{Na^+(g)} \longrightarrow \mathrm{Na^+(aq)}$$
$$\mathrm{NO_3{}^-(g)} \longrightarrow \mathrm{NO_3{}^-(aq)}$$

Hydration *forms* ion-dipole bonds between water molecules and the ion, so exothermic.

Magnitude of enthalpy of hydration: depends on the ion-dipole bond strength between water and the ion in question. Since the dipole of water is a constant here, the ion-dipole bond strength increases when:

- the ions are smaller (up a group)
- the ions have larger charge

Enthalpy of solution $H^{\ominus}_{\text{solution}}$ the enthalpy change when *one mole* of *solid ionic substance* dissolves in water, forming an infinitely dilute solution.

$$\mathrm{NaCl(s)} \longrightarrow \mathrm{NaCl(aq)}$$

$$\begin{tikzcd}
\mathrm{NaCl_{(s)}} \arrow[rr, "\Delta H^{\ominus}_{\text{solution}}"] \arrow[dr, "\Delta H^{\ominus}_{\text{lattice}}"'] & & \mathrm{NaCl_{(aq)}} \\
& \mathrm{Na^+_{(g)} + Cl^-_{(g)}} \arrow[ur, "\Delta H^{\ominus}_{\text{hydration}}"'] &
\end{tikzcd}$$

Using Hess's law: $H^{\ominus}_{\text{solution}} = H^{\ominus}_{\text{lattice}} + H^{\ominus}_{\text{hydration}}$

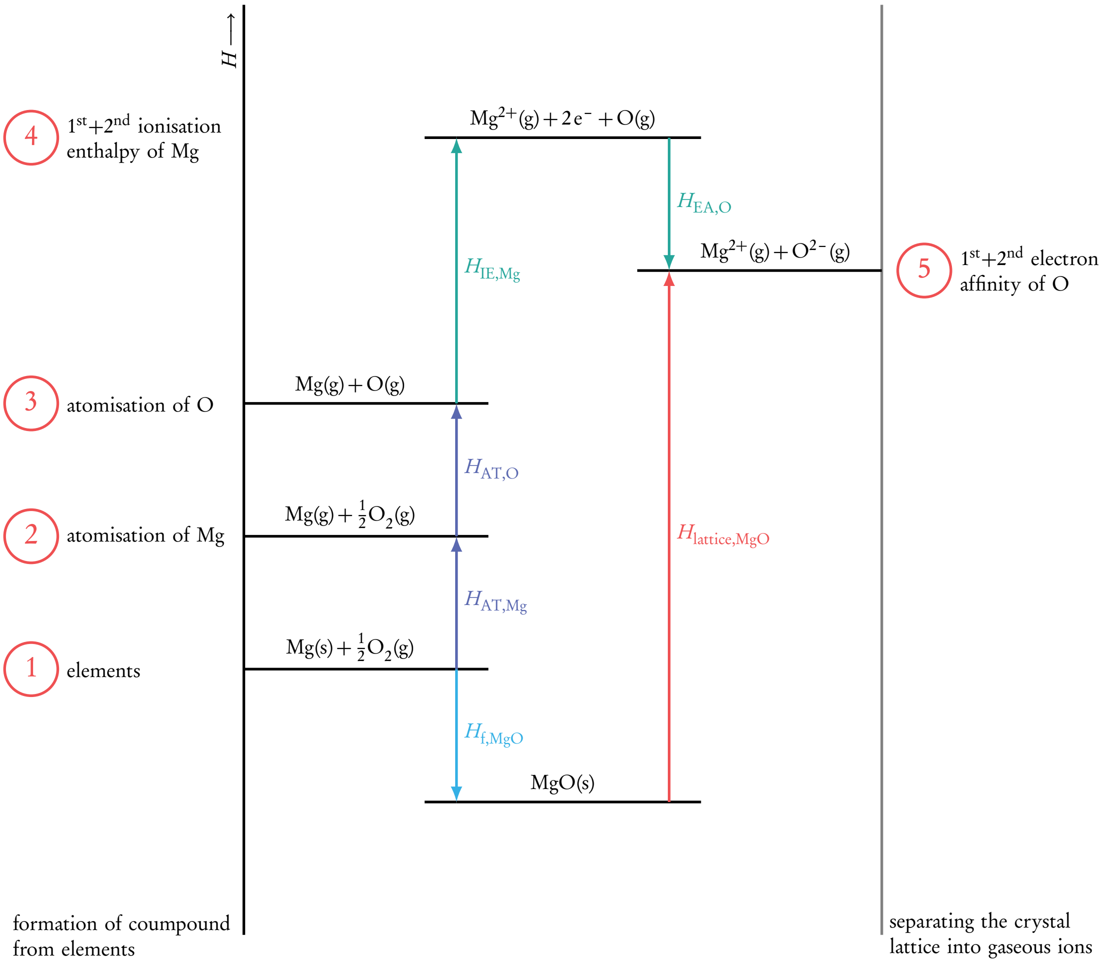
Dissolving can be seen as two seperate processes: breaking all the ionic bonds ($H^{\ominus}_{\text{lattice}}$) and forming ion-dipole bonds with water ($H^{\ominus}_{\text{hydration}}$).

Born-Haber cycles

The amount of energy required to seperate one mole of a solid ionic compound into gaseous ions (under standard conditions) is known as the lattice enthalpy. Under standard conditions ionic bonds are too strong to form free gaseous ions, so lattice enthalpies cannot be determined experimentally. Specialized energy cycles based on Hess's law (Born-Haber cycles) are used to calculate the lattice enthalpy.

Let's study the lattice enthalpy of MgO(s) with the help of figure **??**. The definition of lattice enthalpy is the enthalpy change when one mole of solid ionic compound os separated into gaseous ions: $\mathrm{MgO(s)} \longrightarrow \mathrm{Mg^{2+}(g) + O^{2-}(g)}$.

So let's start at MgO(s) and move toward the free gaseous ions $\mathrm{Mg^{2+}(g) + O^{2-}(g)}$, except instead of moving to the gaseous ions directly we use all the other types of enthalpies to arrive at the free gaseous ions.



From compound ⟶ elements is the reverse of the enthalpy of formation:

① — $-H_{\mathrm{f,MgO}}$ formation of elements from compound

From elements ⟶ gaseous atoms:

② — $+H_{\mathrm{AT,Mg}}$ atomisation of Mg

③ — $+H_{\mathrm{AT,O}}$ atomisation of O

From gaseous atoms ⟶ gaseous ions:

④ — $+H_{\mathrm{1^{st}+2^{nd}IE,Mg}}$ ionisation of Mg

⑤ — $+H_{\mathrm{1^{st}+2^{nd}EA,O}}$ electron affinity of O

Figure 5.6

Using Hess's law, the enthalpy difference between MgO(s) and $Mg^{2+}(g) + O^{2-}(g)$ equals:

$$H_{\text{lattice,MgO}} = -H_{\text{f,MgO}} + H_{\text{AT,Mg}} + H_{\text{AT,O}} + H_{1^{\text{st}}+2^{\text{nd}}\text{IE,Mg}} + H_{1^{\text{st}}+2^{\text{nd}}\text{EA,O}}$$

Importantly, you're not expected to learn this formula by heart. You do have to be able to identify the three steps (reverse of formation, atomisation & ionisation) and predict whether the steps are expected to be exo- or endothermic.

5.6 Entropy

Entropy S refers to the distribution of the available energy among particles. Nature tends toward an increase in entropy, more ways in which the energy can be distributed.

$S = 0$ for: a perfectly ordered crystal at absolute 0 K

Higher entropy: larger disorder, more ways to distribute E, $\Delta S = +$

Lower entropy: more ordered, less ways to distribute E, $\Delta S = -$

Increase entropy of a system

1. **Creation of a gas** disorder increases more during reactions that produce gas compared to the other three factors.
2. **Increased number of particles** disorder increases when a reaction yields an increase in the number of particles.
3. **Change of state** solids have least disorder, liquids/solutions have more disorder, and gases have the most disorder.
4. **Mixing** disorder increases when mixing.

Entropy is also said to quantify the degree of disorder or randomness in a system. Nature tends to an increase in entropy, more disorder.

When predicting entropy changes, a change in the number of *gaseous* particles (1.) is the deciding factor.

Example.

Which reaction has the greatest increase in entropy?

A. $2\,CH_3OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l)$

B. $N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$

C. $2\,HCl(aq) + MgCO_3(s) \longrightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$

D. $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

An increase in entropy corresponds to an increase in disorder. First check reactions wherein the number of *gaseous* molecules increase:

~~A~~. the number of *gaseous* molecules decreases
~~B~~. the number of *gaseous* molecules decreases
C. the number of *gaseous* molecules increases
~~D~~. the number of *gaseous* molecules decreases

Calculate the entropy change ΔS

Calculate the entropy change using DB. 12 and $S^{\ominus}_{\mathrm{H_2}} = 130.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for:

$$\mathrm{CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)}$$

1.	Write the reaction equation	$\mathrm{CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)}$
2.	Find the entropy values (DB. 12)	186 188.8 197.7 130.7
3.	Calculate $\sum S_{\text{reactant}}$ and $\sum S_{\text{product}}$ *seperately*	$\sum S_{\text{reactant}} = 1\times 186 + 1\times 188.8$ $= 375\,\mathrm{J\,K^{-1}\,mol^{-1}}$ $\sum S_{\text{product}} = 1\times 197.7 + 3\times 130.7$ $= 590\,\mathrm{J\,K^{-1}\,mol^{-1}}$
4.	$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$	$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$ $= 590 - 375\,\mathrm{J\,K^{-1}\,mol^{-1}}$ $= 215\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Notice how this calculation is exactly the same as you've done before for the enthalpy of formation.

× number of molecules

NB: the units of S are $\mathrm{J\,K^{-1}\,mol^{-1}}$ and NOT $\mathrm{kJ\,K^{-1}\,mol^{-1}}$

5.6.1 Spontaneity

A reaction will occur spontaneously if a system moves from a less stable to a more stable state. The stability of a system depends *on both the enthalpy change and the entropy change*. These two factors combine to define the standard Gibbs free energy $\Delta G^{\ominus}$:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Standard Gibbs 'free' energy change $\Delta G^{\ominus}$ quantifies the criterion for predicting the spontaneity of a reaction: it is related to both the enthalpy and entropy changes.

$\Delta G < 0$: spontaneous $\Delta G = 0$: equilibrium $\Delta G > 0$: non-spontaneous

$$\Delta G^{\ominus} = \sum G^{\ominus}_{\text{f,products}} - \sum G^{\ominus}_{\text{f,reactants}}$$

Standard Gibbs 'free' energy change of formation $\Delta G_f^{\ominus}$ quantifies the criterion for predicting the spontaneity of the formation of a compound from its elements: it is related to both the enthalpy and entropy changes.

$\Delta G_f^{\ominus} = 0$ for elements under standard conditions

Although S values are *always* positive, the entropy change ΔS of a reaction can be positive or negative. The condition for a spontaneous reaction is as follows:

			Enthalpy	
			exothermic	endothermic
			$\Delta H < 0$	$\Delta H > 0$
Entropy	more disorder	$\Delta S > 0$	$\Delta G = \Delta H - T\,\Delta S$ $\Delta G = (-) - T\,(+)$ always (−), so spontaneous	$\Delta G = \Delta H - T\,\Delta S$ $\Delta G = (+) - T\,(+)$ spontaneous if the $T\Delta S$ term is larger than the ΔH term (high T)
	less disorder	$\Delta S < 0$	$\Delta G = \Delta H - T\,\Delta S$ $\Delta G = (-) - T\,(-)$ spontaneous if the ΔH term is larger than the $T\Delta S$ term (low T)	$\Delta G = \Delta H - T\,\Delta S$ $\Delta G = (+) - T\,(-)$ always (+), so never spontaneous

Calculate the temperature when a reaction becomes spontaneous

At what temperature does the following reaction become spontaneous?

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g) \qquad \Delta H = 179\,\mathrm{kJ\,mol^{-1}}$$

Substance	$S^{\ominus}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$
$CaCO_{3(s)}$	92.9
$CaO_{(s)}$	39.8
$CO_{2(g)}$	213.7

× number of molecules

1.	Calculate the change in entropy: $\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$	$\Delta S = (1 \times 213.7 + 1 \times 39.8) - 1 \times 92.9$ $= 160.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$
2.	Convert to $\mathrm{kJ\,K^{-1}\,mol^{-1}}$ (to match $\Delta\mathrm{H}$)	$= 0.1606\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$
3.	Write the expression for ΔG and equate it to zero.	$\Delta G = \Delta \mathrm{H} - T\Delta \mathrm{S} = 0$
4.	Rearrange to calculate minimum value of T.	$T\Delta S = \Delta H$ $T = \dfrac{\Delta H}{\Delta S}$
	Substitute ΔH and ΔS.	$= \dfrac{+179}{0.1606} = 1114\,\mathrm{K}$
5.	At T greater than the result, the reaction will be spontaneous.	The reaction will be spontaneous at $T > 1114\,\mathrm{K}$

KINETICS

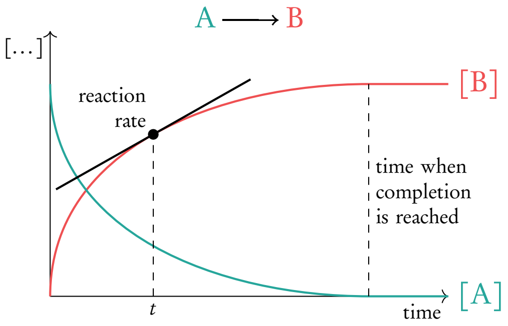
6

Reaction rate the change in concentration of a particular reactant or product per unit time, measured in mol dm^{-3} s^{-1}

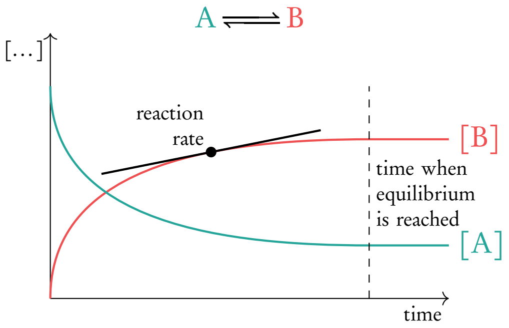
$$\text{rate} = -\frac{\Delta[\text{reactants}]}{\Delta t} = \frac{\Delta[\text{products}]}{\Delta t}$$

In a concentration vs. time graph, which shows the progress of a chemical reaction, the reaction rate is equal to the tangent or slope. When the slope = 0 (the graph is horizontal) the reaction has reached either completion or equilibrium.

Completion



Equilibrium



Experimental determination

The rate of reaction can be experimentally determined by measuring how the concentration *changes* with time. Multiple concentration measurements have to be performed over time to infer the rate from the change. To measure concentration we can:

- use an absorption spectrometer; absorption is stronger with a higher concentration (of for example coloured transition metals complexes)
- measure the pH if the [H$^+$] or [OH−] concentrations change
- measure the electrical conductivity if the ionic concentration changes
- measure the volume of a gas (which is proportional to the amount in mole) that is evolved from reaction
- measure the mass change of the sample as a result of gas formation.

6.1 Collision Theory

Collision theory states the three conditions that must be met for a succesful reaction to take place:

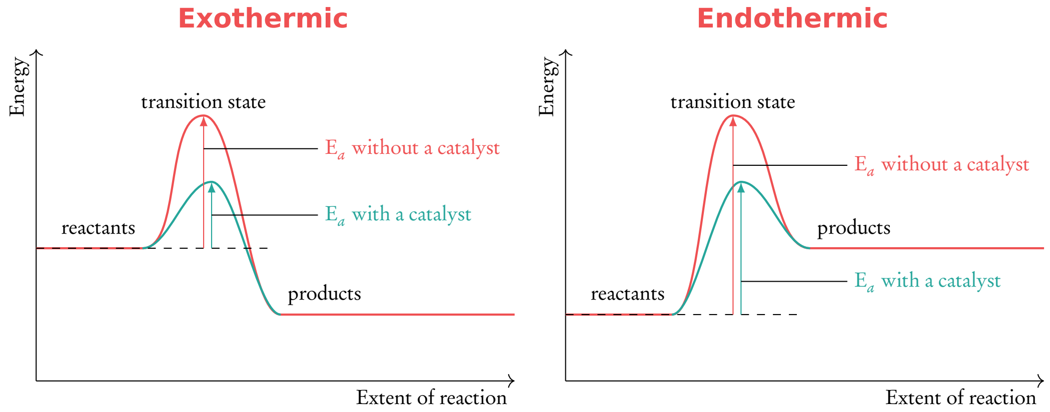
	Collision theory	increase rate
1	particles must collide,	higher collision frequency
2	with proper orientation,	—
3	and sufficient energy	increase collision energy (by increasing T), lower energy barrier (E_a)

The collision theory can be used to understand how the rate of reaction can be affected. Every collision with proper orientation and with sufficient energy leads to a chemical reaction (known as **effective collisions**). When more collisions occur per second (*higher collision frequency*), there is a proportional increase in the number of effective collisions. Also, by either increasing the collision energy or lowering the energy barrier, a *larger fraction* of the collisions are effective. The orientation of collisions is random and cannot be influenced.

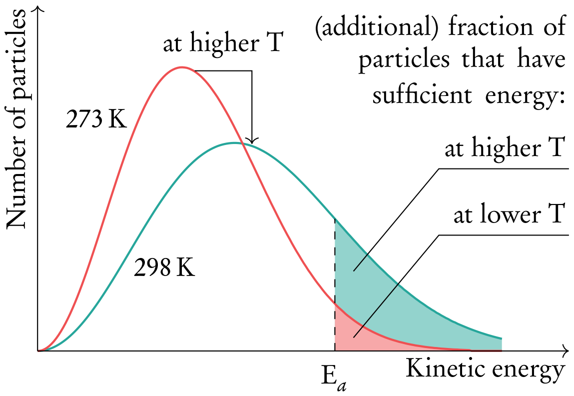
The four factors that increase the rate of reaction:

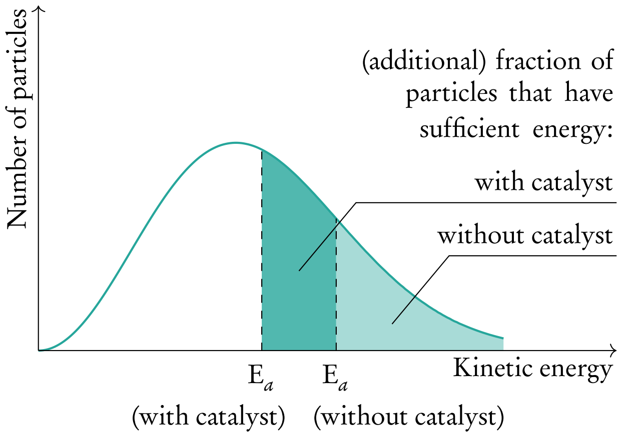
or decrease by doing the opposite

1. **↑ concentration/pressure:** particles are closer together so the *collision frequency* will increase.
2. **↑ surface area / ↓ particle size:** collisions with solids occur on the surface, so increasing the surface area will increase the *collision frequency*.
3. **↑ temperature:** particles have a higher amount of average kinetic energy, resulting in an increase in the *collision frequency* **and** a *larger fraction* of the collisions will be effective by increasing the collision energy.
4. **add catalyst:** provides an alternative reaction pathway/mechanism which has a lower activation energy, so a *larger fraction* of the collisions will be effective.



The activation energy (E_a) is the minimum amount of energy of a collision between two particles to lead to a reaction. We can say: the energy required for an effective collision.





6.2 Rate equation and reaction order

The rate equation shows the mathematical relation between the concentrations of reactants and the rate of the reaction. When A and B react:

Rate equation: rate $= k[A]^x[B]^y$

x is the order of the reaction with respect to A, and y with respect to B.

The overall order of reaction: $= x + y$.

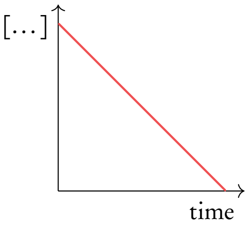
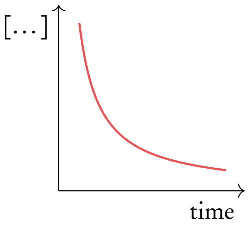
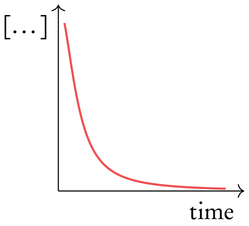
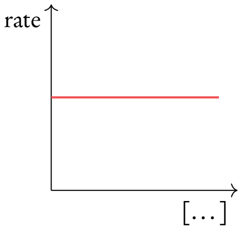
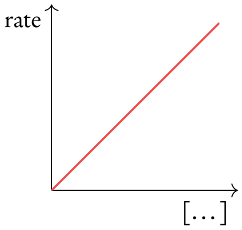
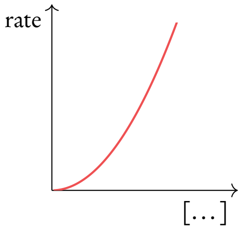
Note: the order of the reaction (and therefore also the rate equation) can *only* be derived from:

1. experimental data or
2. from the reaction mechanism if the rate determining step (r.d.s.) is known.

It *cannot* be derived from the balanced reaction equation!

Order of a reaction

The order of reaction conveys the mathematical dependence of the rate on the concentration of the reactant. To simplify things, let's assume there is only reactant A and x is the overall order. The rate equation can be written as: $\text{rate} = k[\text{A}]^x$.

	zero order	first order	second order
rate equation	$\text{rate} = k^{*1}$	$\text{rate} = k[\text{A}]$	$\text{rate} = k[\text{A}]^2$
[. . .] vs time			
rate vs [. . .]			
units of k^{*2}	$k = \text{rate}$ $= \text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$	$k = \dfrac{\text{rate}}{[\text{A}]}$ $= \dfrac{\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}}{\text{mol}\,\text{dm}^{-3}}$ $= \text{s}^{-1}$	$k = \dfrac{\text{rate}}{[\text{A}]^2}$ $= \dfrac{\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}}{(\text{mol}\,\text{dm}^{-3})^2}$ $= \text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}$

The rate is equal to the slope of [. . .] vs time. And note that while the reaction rate decreases over time (for the first and second order graphs), the greater concentration causes the rate to increase.

---

*1 Since $k[\text{A}]^0 = k$

*2 The units of the rate constant depend on the overall order of the reaction. Solving for k yields $k = \dfrac{\text{rate}}{[\text{A}]^x}$.

Derive the rate equation from experimental data

To derive the order of the reaction, the rate of reaction is measured at varying reactant concentrations. Keeping all reactant concentrations the same except that of [A], the rate $\propto [A]^x$:

		zero order $x = 0$	first order $x = 1$	second order $x = 2$	third order $x = 3$
double [A]	rate $\propto 2^x$	rate doesn't change	rate $\times 2^1 = \times 2$	rate $\times 2^2 = \times 4$	rate $\times 2^3 = \times 8$
triple [A]	rate $\propto 3^x$	rate doesn't change	rate $\times 3^1 = \times 3$	rate $\times 3^2 = \times 9$	rate $\times 3^3 = \times 27$

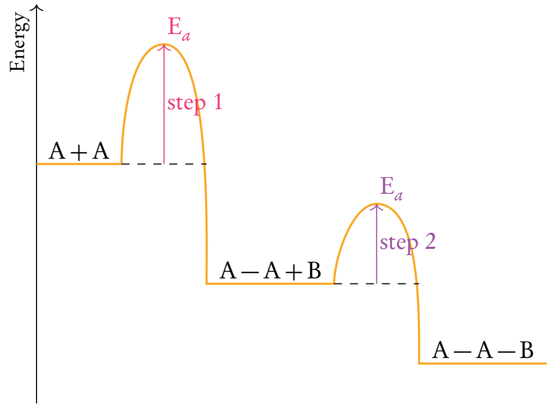
Derive the rate equation from a reaction mechanism

Since the collision of more than two particles with the correct orientation and sufficient energy is *extremely* unlikely, many reactions proceed in multiple steps. The step by step sequence of elementary reactions by which the overall chemical change occurs is called the **reaction mechanism**.

A successful collision between two molecules can lead to an **activated intermediate**, which can continue to form the product in a subsequent collision, or revert back to the original reactants.

Let's study the reaction $2\,A + B \longrightarrow A{-}A{-}B$. A possible mechanism is:

step 1. $A + A \rightleftharpoons A - A$
step 2. $A - A + B \longrightarrow A - A - B$



From the energy diagram we see that the activation energy of step 1. is higher than the activation energy of step 2. This means that the rate of step 1. will be slower than that of step 2. The rate of the overall reaction is determined by the slowest step in a reaction mechanism, known as the **rate determining step (r.d.s.)**. The overall reaction rate will therefore only depend on the formation of A—A, so the rate $= k[A][A] = k[A]^2$.

A rate equation can be written for every **elementary step**. The overall rate of reaction depends on the r.d.s., so when the rate equation of the r.d.s. contains an intermediate it should be replaced by the (previous) rate equation in which the intermediate is formed.

	Mechanism	Rate equation	Molecularity
step 1.	$A + B \xrightarrow{\text{fast}} X$	$\text{rate} = k[A][B]$	bimolecular
step 2.	$A + X \xrightarrow{\text{slow}} Y$	$\text{rate} = k[A][X]$	bimolecular
step 3.	$Y \xrightarrow{\text{fast}} C + D$	$\text{rate} = k[Y]$	unimolecular
overall	$2A + B \longrightarrow C + D$	$\text{rate} = k[A][X] = k[A][A][B]$	

Find the rate equation when the reaction mechanism and r.d.s. are known.

Determine the rate equation given the following mechanism for $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$:

$$\begin{array}{ll} \text{step 1.} & NO + NO \overset{\text{fast}}{\rightleftharpoons} N_2O_2 \\ \text{step 2.} & N_2O_2 + H_2 \xrightarrow{\text{slow}} N_2O + H_2O \\ \text{step 3.} & N_2O + H_2 \xrightarrow{\text{fast}} N_2 + H_2O \end{array}$$

1.	Determine the rate equation of the r.d.s.	$\text{rate} = k[N_2O_2][H_2]$
2.	If the rate equation contains and intermediate product, replace it with the [reactants] that form the intermediate.	N_2O_2 is an intermediate (it is not present in the overall reaction), so replace $[N_2O_2]$ with $[NO][NO]$. $\text{rate} = k[NO][NO][H_2] = k[NO]^2[H_2]$
3.	Repeat step 2 if there is still an intermediate product	NO and H_2 are both reactants in the overall reaction, no repeat necessary
4.	Write down the rate equation	$\text{rate} = k[NO]^2[H_2]$

Arrhenius equation

The rate constant k depends *only* on the temperature for a particular reaction. The Arrhenius equation relates the rate constant k with the absolute temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

k	= rate constant	depends
A	= frequency factor	depends
E_a	= activation energy	[J]
R	= gas constant	$[8.31\,\mathrm{J\,K^{-1}}]$
T	= temperature	[K]

This equation is often written in its logarithmic form, which can be viewed as a linear equation by adapting the x and y-axis:

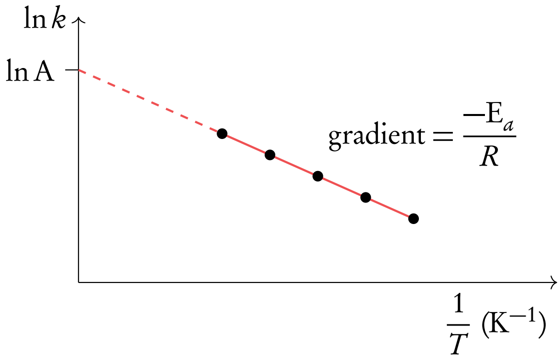
$$\begin{aligned}\ln k &= \frac{-E_a}{RT} + \ln A \\ &= \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A \\ &= m \cdot x + c\end{aligned}$$

If $\ln k$ is plotted on the y-axis, and $\frac{1}{T}$ on the x-axis:

- then the slope (m) equals $\frac{-E_a}{R}$
- and the intersection with the y-axis (c) equals $\ln A$, and

So when k is measured at different temperatures, and the results are plotted in a $\ln k$ vs $\frac{1}{T}$ graph, then:

- the activation energy can be calculated from the slope ($\frac{-E_a}{R}$), and
- the frequency factor A can be calculated from exptrapolation to the $\ln k$-axis.



You can solve simultaneous equations when you know k at two different temperatures, using the following equation from the databook:

$$\ln \frac{k_1}{k_2} = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

EQUILIBRIUM

7

7.1 Dynamic equilibrium

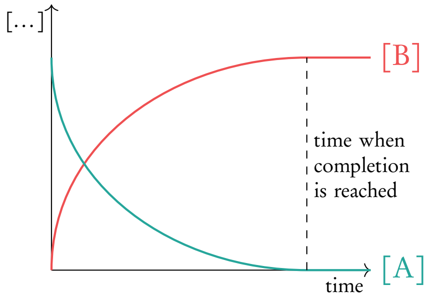
In a static equilibrium nothing changes, like for example in a mass balance. Chemical equilibriums are dynamic, there is a constant conversion in both directions such that there is no *net change*.

Dynamic equilibrium the *forward rate* of reaction equals the *reverse rate* of reaction.

Note that the *amounts* of reactants and products are not (necessarily) equal, the amounts are constant / do not change.

Completion reaction

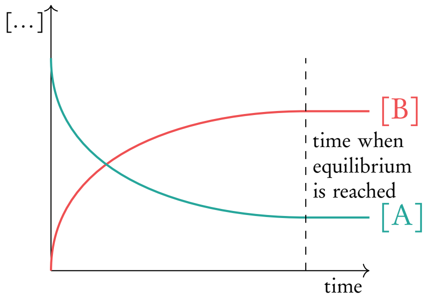
$$A \longrightarrow B$$



Reaction stops when the limiting reagent runs out.

Equilibrium reaction

$$A \rightleftharpoons B$$



Reaction continues indefinitely but reaches equilibrium.

A system at equilibrium is a mixture with all of the reactants and products present*, and the concentrations of the reactants and the products do not change. A consequence is that the macroscopic properties (the colour, viscosity etc.) of the system does not change. Systems can only remain in equilibrium in a closed system, since the exchange of matter with the surroundings would disturb the equilibrium.

*remember: usually not in equal amounts!

Understanding equilibriums

Using Collision Theory, we know that the reaction rate depends on the concentration. The forward reaction rate is proportional to the [reactant], and the reverse reaction rate is proportional to [product].

$$\text{reactant} \underset{\text{rate} \propto [\text{product}]}{\overset{\text{rate} \propto [\text{reactant}]}{\rightleftharpoons}} \text{product}$$

At the time that reagents are mixed ($t = 0$) the forward reaction rate is greatest, but it decreases over time as the [reactant] decreases. At $t = 0$ the reverse reaction rate is 0, as $[\text{product}] = 0$. But as [product] increases over time, so will the reverse reaction rate.

At equilibrium the forward reaction rate has decreased and the reverse reaction rate has increased to the point that they are *equal*. It does not matter from which side the equilibrium is approached, at some point the two rates will be equal.

7.2 Equilibrium law expression

Consider the generic chemical reaction given below, in which $A + B$ react to form $C + D$ and the reaction coefficients are indicated by the small letters $pqrs$.

$$pA + qB \rightleftharpoons rC + sD$$

The reaction quotient Q is defined at any point in time during the reaction as:

$$Q = \frac{[C]^r \times [D]^s}{[A]^p \times [B]^q} = K_c \qquad \text{or abstractly as} \qquad \frac{[\text{products}]}{[\text{reactants}]}$$

Since the concentrations of the reactants and products do not change at equilibrium, the reaction quotient Q has a very specific value, which is called the equilibrium constant K_c (which *only* depends on temperature).

Determine if a system is at equilibrium / predict direction of shift to restore equilibrium

Sulphurdioxide reacts with oxygen forming sulphurtrioxide in an equilibrium reaction. At the prevailing temperature all substances are gaseous and $K_c = 2$. At some point in time, the concentrations are $[SO_2] = 2\,M$, $[O_2] = 1\,M$ and $[SO_3] = 2\,M$. Determine if the system is at equilibrium and predict direction of the shift to restore equilibrium.

1.	Write down the balanced equilibrium reaction.	$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
2.	Derive the reaction quotient Q and calculate the result.	$Q = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$ $= \frac{2^2}{2^2 \times 1} = 1$
3.	When the equilibrium point is reached $Q = K_c$.	Since $Q = 1$ at the given point in time, $Q \neq K_c$, so the system is *not* in equilibrium.
4.	Use $Q = \frac{[\text{product}]}{[\text{reactant}]}$. If $Q > K_c$ shift to reactant side and if $Q > K_c$ shift to product side.	Since $Q < K_c$ at the given point in time, to restore equilibrium the value of Q should increase by increasing the [product] / [reactant] , so the system is *not* in equilibrium.

Magnitude of $K_c = \frac{[\text{products}]}{[\text{reactants}]}$

If K_c has a very large value then the [product] must be much higher then the [reactant]. In summary for all values of K_c:

	reaction
$K_c \ll 1$	(almost) no reaction
$K_c < 1$	equilibrium favours reactant side
$K_c \approx 1$	approx. equal [reactant] and [product]
$K_c > 1$	equilibrium favours product side
$K_c \gg 1$	tends to completion

Manipulation of K_c

When an equilibrium reaction is reversed, the equilibrium constant is inversed $(\frac{1}{K_c})$. And when chemical reactions are added up together their respective equilibrium constants are multiplied $(K_{c1} \times K_{c2})$.

Reversal: when discussing equilibrium reactions the terms reactant side and product side are often avoided, since it is a matter of perspective. For example, in the equilibrium of $2NO_2 \rightleftharpoons N_2O_4$ the following reactions occur at the same time:

- $2NO_2 \longrightarrow N_2O_4$
- $N_2O_4 \longrightarrow 2NO_2$

Both equilibrium reactions $2NO_2 \rightleftharpoons N_2O_4$ and $N_2O_4 \rightleftharpoons 2NO_2$ represent the same equilibrium. What is the forward reaction in the one representation of the equilibrium, is the reverse reaction in the other. The equilibrium law expression of the two reactions are each others inverse:

	$2NO_2 \rightleftharpoons N_2O_4$	$N_2O_4 \rightleftharpoons 2NO_2$
equilibrium law expression	$K_c = \frac{[N_2O_4]}{[NO_2]^2}$	$K_c{}' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K_c}$

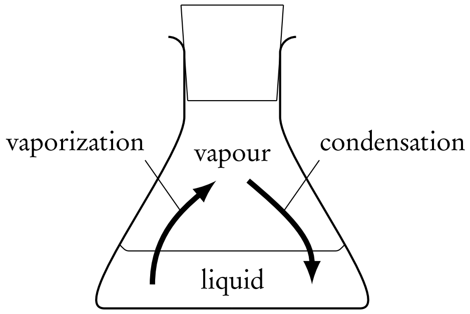
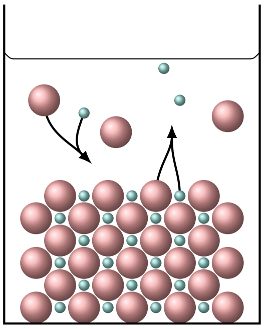
Addition: when multi-step reactions are added to give an overall reaction, the increase of a reaction coefficient cause the power in the quotient Q to increase. This means that when reactions are added, the quotients are multiplied:

step 1.	$A + B \rightleftharpoons X$	$K_{c1} = \frac{[X]}{[A][B]}$
step 2.	$A + X \rightleftharpoons C$	$K_{c2} = \frac{[C]}{[A][X]}$
overall	$2A + B \rightleftharpoons C$	$K_{c\text{overall}} = K_{c1} \times K_{c2} = \frac{\cancel{[X]}[C]}{[A][B][A]\cancel{[X]}} = \frac{[C]}{[A]^2[B]}$

So the multiplication of the equilibrium expressions indeed leads to the correct equilibrium expression of the overall reaction.

7.3 States of matter

So far we've only considered chemical equilibriums in closed systems, but similarly we can consider physical states of matter in closed systems. In particular: liquid-vapour equilibrium and precipitation-solution equilibrium of ionic compounds.

	Liquid vapour equilibrium	Solution equilibrium
Equilibrium	$H_2O(l) \rightleftharpoons H_2O(g)$.	$NaCl(s) \rightleftharpoons NaCl(aq)$
Drawing		
Explanation	Fast moving particles will escape the liquid phase, evaporating into vapour phase. While slow moving particles condense into the liquid phase. When the rates of these processes are equal, a dynamic equilibrium will establish.	The ability of an ionic compound to dissolve depends on the rates of solution and precipitation, or in other words by the hydration vs the lattice enthalpies. While table salt dissolves fully up to the point of saturation, the rates of solution and precipitation are at equilibrium after a solution is saturated.
Independent of:	– Surface area: affects both evaporation and condensation – Volume of liquid in container	– Surface area: affects both solution and precipitation – Volume of solid in container
Dependent on:	– Volume of gas in container (concentration or partial pressure)	– Volume of liquid in container (concentration of dissolved particles)

7.4 Le Chatelier's principle

Le Chatelier's principle states how a system that is in equilibrium responds to an external change.

Le Chatelier's principle when a system at equilibrium is disturbed by changing the conditions, the system will shift the position of equilibrium to (partially) couteract the change.

Factors that affect the equilibrium position

The factors that affect the equilibrium position will be exemplified based on the following generic chemical reaction:

$$3A(g) + B(s) \rightleftharpoons 3C(g) + D(g) \qquad \Delta H = -195\,\mathrm{kJ\,mol^{-1}}$$

Stress	The position of the equilibrium will:	Example
increase $[A]$	shift away from A in order to lower $[A]$	to the product side
decrease $[D]$	shift towards D to partially restore its concentration	to the product side
increase P by a decrease in V	shift towards the side with fewer **gaseous** molecules to reduce the pressure	so to the reactant side
increase P by addition of an inert gas	no effect, because the partial pressures of the reactants and products do not change	–
add a catalyst	no effect, because the forward and reverse reaction rates are increased equally	–
increase T	shift toward the endothermic side (to lower the temperature) **by changing the value of K_c**	to the reactant side, since the forward reaction is exothermic ($\Delta H = -$)

7.5 Equilibrium calculations

Completion reaction

- Reaction continues until the limiting reactant is fully consumed.

Equilibrium reaction

- Reaction occurs in both directions simultaneously.
- At equilibrium the amounts are constant

In equilibrium calculations we always use the RICE table and the equilibrium law expression ($K_c = \ldots$). The concept of limiting reactant is invalid in equilibrium reactions.

Equilibrium calculations

$2.0\,\text{mol}$ $H_2(g)$ and $1.0\,\text{mol}$ $N_2(g)$ react in equilibrium, forming $NH_3(g)$. The volume of the closed container is $2.0\,\text{dm}^3$ and the temperature is kept constant. At equilibrium, $0.50\,\text{mol}$ of $NH_3(g)$ is present.

Calculate the value of the equilibrium constant K_c.

1. Convert the given values to concentrations.

Indicate $[\ldots]_{in}$ or $[\ldots]_{eq}$

$$[H_2]_{in} = \frac{2.0\,\text{mol}}{2.0\,\text{dm}^3} = 1.0\,\text{mol}\,\text{dm}^{-3}$$

$$[N_2]_{in} = \frac{1.0\,\text{mol}}{2.0\,\text{dm}^3} = 0.50\,\text{mol}\,\text{dm}^{-3}$$

$$[NH_3]_{eq} = \frac{0.50\,\text{mol}}{2.0\,\text{dm}^3} = 0.25\,\text{mol}\,\text{dm}^{-3}$$

2. Write the balanced equilibrium reaction and use it as a header for a RICE table.

Change: use x & reaction coefficients

Reaction	$3H_2(g)$	$+$	$N_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial					
Change	$-3x$		$-x$		$+2x$
Equilibrium					

3. Complete the table, *use concentrations*

Initial: check the text, 0 when unknown
Equilibrium = Initial + Change

Reaction	$3H_2(g)$	$+$	$N_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initial	1.0		0.50		0
Change	$-3x$		$-x$		$+2x$
Equilibrium	$1.0-3x$		$0.5-x$		$2x(=0.25)$

4. K_c is unknown: use $[\ldots]_{eq}$ to calculate x and calculate all *values* in Equilibrium

K_c is known: insert the *expressions* from Equilibrium into $K_c = \ldots$

$[NH_3]_{eq}$ is known, so $2x = 0.25$ and $x = 0.125$

$$[H_2]_{eq} = 1.0 - 3 \cdot 0.125 = 0.625\,\text{mol}\,\text{dm}^{-3}$$

$$[N_2]_{eq} = 0.5 - 0.125 = 0.375\,\text{mol}\,\text{dm}^{-3}$$

5. Write $K_c = \ldots$ and plug in the *values or expressions* of the Equilibrium amounts. Make sure to answer the question.

$$K_c = \frac{[NH_3]^2}{[H_2]^3 \cdot [N_2]} = \frac{(0.25)^2}{(0.625)^3(0.375)} = 0.68$$

7.6 Relation between ΔG and K_c

The position of equilibrium corresponds to: a maximum value of entropy and a minimum in the value of the Gibbs free energy change.

ΔG and $\mathrm{K_c}$ are related by (from DB 1):

$$\Delta G = -RT \ln \mathrm{K_c}$$

ΔG = free energy change [$\mathrm{J\,mol^{-1}}$]
R = gas constant [$8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$]
T = temperature [K]
$\mathrm{K_c}$ = equilibrium constant depends

$$\ln \mathrm{K_c} = -\frac{\Delta G}{RT}$$

$$e^{\ln \mathrm{K_c}} = e^{-\frac{\Delta G}{RT}}$$

$$\mathrm{K_c} = e^{-\frac{\Delta G}{RT}}$$

in order to rewite $\Delta G = -RT \ln \mathrm{K_c}$ to make $\mathrm{K_c}$ the subject, first $\ln \mathrm{K_c}$ is isolated on one side.

The inverse function of ln is: e to the power.

From this equation we can infer that:

- the larger ΔG (positive value), the smaller $\mathrm{K_c}$ will to be.
- the opposite
- and since $e^0 = 1$, when $\Delta G = 0$ then $\mathrm{K_c} = 1$.

Since ΔG and $\mathrm{K_c}$ are related, they are both indicators for the position of equilibrium and for the sponteneity of reactions.

	reaction		reaction
$\mathrm{K_c} \ll 1$	(almost) no reaction	$\Delta G \gg 0$	non-spontaneous
$\mathrm{K_c} < 1$	equilibrium favours reactant side	$\Delta G > 0$	non-spontaneous
$\mathrm{K_c} \approx 1$	approx. equal [reactant] and [product]	$\Delta G \approx 0$	equilibrium
$\mathrm{K_c} > 1$	equilibrium favours product side	$\Delta G < 0$	spontaneous
$\mathrm{K_c} \gg 1$	tends to completion	$\Delta G \ll 0$	spontaneous

ACIDS AND BASES

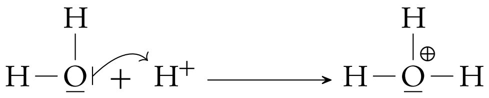
8

8.1 Acid and base definitions

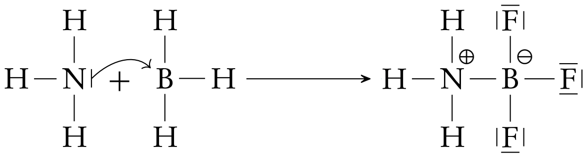
An alkali is a base that is soluble in water

	Brønsted-Lowry	Lewis
Acid	H^+ donor	e^--pair acceptor
Base	H^+ acceptor	e^--pair donor
Amphoteric	H^+ donor & acceptor	e^--pair donor & acceptor
Amphiprotic	H^+ donor & acceptor	—

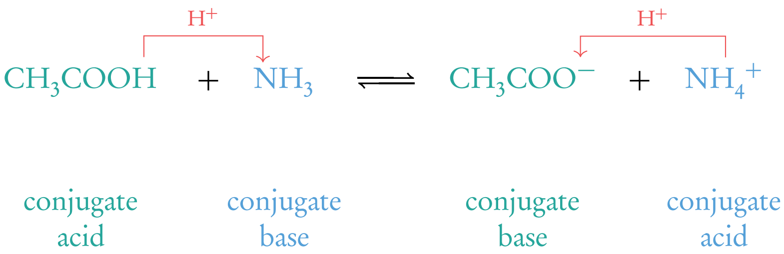
Every Brønsted-Lowry acid & base is also a Lewis acid and base:



But some Lewis acids and bases are not Brønsted-Lowry acids and bases:



Conjugate acid/base pair a pair of molecules that differ by a single H^+-ion



So the **conjugate base** is the species formed after the acid has donated a proton, and the **conjugate acid** is the species formed after the base has accepted a proton.

8.2 Strong vs weak

Strong acid/base completely dissociates into its ion in aqueous solution

Strong acid $HCl + H_2O \longrightarrow Cl^- + H_3O^+$

Strong base $NaOH \longrightarrow Na^+ + OH^-$

100 %

A proton in solution can be written as H^+ or H_3O^+.

Weak acid/base dissociates partially into its ion in aqueous solution

Weak acid $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Weak base $NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$

$\approx 1\,\%$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]\cancel{[H_2O]}} \qquad K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]\cancel{[H_2O]}}$$

In solution, the $[H_2O]$ barely changes due to the reaction, so we assume it stays constant. K_a/ K_b incorporates its value.

	Common acids		Common bases		
Strong	HCl	hydrochloric acid			
	H_2SO_4	sulfuric acid			
	HNO_3	nitric acid			
Weak	H_3PO_4	phosphoric acid	$H_2PO_4{}^-$	dihydrogen phosphate	Weak
	CH_3COOH	ethanoic acid	CH_3COO^-	ethanoate	
	H_2CO_3	carbonic acid	$HCO_3{}^-$	hydrogen carbonate	
	$HCO_3{}^-$	hydrogen carbonate	$CO_3{}^{2-}$	carbonate	
	$CH_3NH_3{}^+$	methyl ammonium	CH_3NH_2	methane amine	
	$NH_4{}^+$	ammonium	NH_3	ammonia	
			OH^-	hydroxide	Strong
			O^{2-}	oxide	
			$C_2H_5O^-$	ethoxide	

Any carboxylic acid is a weak acid, and the conjugate base (carboxylate) a weak base.

Any amine is a weak base, and the conjugate acid (ammonium) a weak acid.

The strong bases occur on the exam as metal salts, such as NaOH, KOH, . . .
and Na_2O, K_2O, . . .

Experiments to distinguish strong and weak

The difference between strong and weak is the amount of dissociation into ions. An *equimolar* amount (!) of a strong acid will have a larger $[H_3O^+]$ *than the same amount* of a weak acid. The same holds for bases, but then the strong base will have a larger $[OH^-]$.

1. **pH measurement** – strong acids have higher $[H_3O^+]$ so the pH will be lower than that of a weak acid, and the reverse holds for strong bases. The pH can be measured with a digital pH meter, or with a (universal) indicator.
2. **Conduction measurement** – strong acids/bases dissociate fully into ions, so the conductivity of the solution will be much higher.
3. **Reaction rate** – strong acids have higher $[H_3O^+]$, so the reaction rate will be higher. For example: an equimolar amount of strong acid will produce a more vigorous reaction with a reactive metal than a weak acid.

Typical reactions of acids for which observations can be made include:

Reaction type	Example reaction	Observation
neutralisation	$2HCl + Na_2O \longrightarrow 2NaCl + H_2O$	exothermic, so the T ↑
metals (redox)	$2HCl + Mg \longrightarrow MgCl_2 + H_2$	H_2(g) bubbles
carbonate	$2HCl + Na_2CO_3 \longrightarrow 2NaCl + CO_2 + H_2O$	CO_2(g) bubbles
hydrogen carbonate	$HCl + NaHCO_3 \longrightarrow NaCl + CO_2 + H_2O$	CO_2(g) bubbles

Important distinctions

Strong fully dissociated into ions

Weak partially dissociated to ions

Concentrated solution with a high concentration

Dilute solution with a low concentration

Corrosive highly reactive chemical

TWO factors that affect the pH/pOH of a solution the strength of the acid or base (strong vs weak) **AND** the concentration of the acid or base

A highly concentrated solution of a weak acid can easily be more acidic than a dilute solution of a strong acid.

8.3 pH scale

Self ionosation of water

The $[H_2O]$ barely changes since the equilibrium lies far to the left, so we assume it stays constant. K_w incorporates its value.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad \Delta H = +57\,\mathrm{kJ\,mol^{-1}}$$

Due to the self-ionisation of water, the $[H_3O^+]$ and $[OH]$ are inversely proportional and can be calculated by the following formulas:

$$\begin{aligned} K_w &= [H_3O^+]\cdot[OH^-] && = 10^{-14} && \text{at } 298\,\mathrm{K} \\ pK_w &= pH + pOH && = 14.00 && \text{at } 298\,\mathrm{K} \end{aligned}$$

Example.

Determine the $[H_3O^+]$ and the pH of pure water at 373 K.

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

1. The only source of H_3O^+ and OH^- in pure water is from self ionisation. This means that the $[H_3O^+] = [OH^-] = x$.
2. The value of Kdepends on the temperature. In DB table 23 the K_w values are listed: $K_w = 56.0 \times 10^{-14}$ at $373\,\mathrm{K} = 100\,°\mathrm{C}$.

$$K_w = [H_3O^+][OH^-]$$
$$56.0 \times 10^{-14} = x^2$$
$$x = \sqrt{56.0 \times 10^{-14}} = 2.37 \times 10^{-7}$$

Remember what x means in the equation:
$x = [H_3O^+] = [OH^-] = 2.37 \times 10^{-7}\,\mathrm{mol\,dm^{-3}}$. So at 373 K the $pH = -\log 2.37 \times 10^{-7} = 6.626$. This solution with equal amounts of $[H_3O^+]$ and $[OH^-]$ is neutral at $pH = 6.625$.

Neutral solution
solution that contains equal amounts of H_3O^+ and OH^-

Acidic solution (at 298 K $pH < 7$)
solution that contains H_3O^+ (more than OH^-)

Alkaline solution (at 298 K $pH > 7$)
solution that contains OH^- (more than H_3O^+)

pH scale

pH stands for potential of Hydrogen, which is a scale to specify the acidity or basicity of an aqueous solution. The scale is logarithmic, so a change of **one unit in pH** represents a **10-fold change in concentration**.

Formula to calculate p…

$$pH = -\log[H_3O^+]$$

$$pOH = -\log[OH^-]$$

Inverse to calculate […]

$$[H_3O^+] = 10^{-pH}$$

$$[OH^-] = 10^{-pOH}$$

	pH	$[H_3O^+]$	$[OH^-]$	pOH	
	…	…	…	…	
acidic	-1	10^{1}	10^{-15}	15	acidic
	0	10^{0}	10^{-14}	14	
	1	10^{-1}	10^{-13}	13	
	…	…	…	…	
	6	10^{-6}	10^{-8}	8	
neutral	7	10^{-7}	10^{-7}	7	neutral
	8	10^{-8}	10^{-6}	6	
	…	…	…	…	
	13	10^{-13}	10^{-1}	1	
	14	10^{-14}	10^{0}	0	
alkaline	15	10^{-15}	10^{1}	-1	alkaline
	…	…	…	…	

Contrary to popular belief, the pH value can be less than 0 or greater than 14 for *very strong and highly concentrated* acids and bases.

So: +1 on the pH scale corresponds to a 10× larger $[H_3O^+]$

8.4 pH calculations

pH formulas important to memorize. Fortunately they are very similar:

Formulas to calculate p…	Inverse to calculate …
$pH = -\log[H_3O^+]$	$[H_3O^+] = 10^{-pH}$
$pOH = -\log[OH^-]$	$[OH^-] = 10^{-pOH}$
$pK_a = -\log K_a$	$K_a = 10^{-pK_a}$
$pK_b = -\log K_b$	$K_b = 10^{-pK_b}$
$pK_w = -\log K_w$	$K_w = 10^{-pK_w}$

K_w equals …	pK_w equals …
$K_w = [H_3O^+] \cdot [OH^-]$	$pK_w = pH + pOH$
$= K_a \cdot K_b$	$= pK_a + pK_b$
$= 1 \times 10^{-14}$ at 298 K	$= 14.00$ at 298 K

pH calculations: strong acids and bases

Calculate the pH of a $0.500\,mol\,dm^{-3}$ Na_2O-solution

1.	Write the r.eq. of acid OR base with H_2O	$Na_2O + H_2O \longrightarrow 2\,Na^+ + 2\,OH^-$
2.	Use molar ratios to determine the $[H_3O^+]$ or $[OH^-]$	The molar ratio of $Na_2O : OH^- = 1 : 2$. So: $[OH^-] = 2 \cdot 0.500 = 1.00\,mol\,dm^{-3}$
3.	Answer the question (by using the pH formulas)	$pOH = -\log[OH^-]$ $= -\log 1.00\,mol\,dm^{-3} = 0.00$ $pH = 14.00 - 0.00 = 14.00$

pH calculations: weak acids and bases

Calculate the pH of a $0.500\,\mathrm{mol\,dm^{-3}}$ CH_3COOH-solution

1.	Write the r.eq. of acid OR base with H_2O	$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
2.	Write $K_a = \ldots$ or $K_b = \ldots$	$K_a = \dfrac{[CH_3COO-][H_3O^+]}{[CH_3COOH]}$
3.	Equate the expression to: $K = \dfrac{x^2}{M - x}$ where $x = [H_3O^+]$ or $[OH^-]$ and $M =$ the initial [acid] or [base]	$K_a = \dfrac{[CH_3COO-][H_3O^+]}{[CH_3COOH]}$ $= \dfrac{x^2}{[CH_3COOH]_0 - x}$
4.	Of three variables, two must be given: 1. K_a or K_b from values in the DB 2. the initial $[\text{acid}]_0$ or $[\text{base}]_0$ 3. $x = [H_3O^+]$ or $[OH^-]$, can be calculated from the pH	From DB: $pK_a = 4.76$ for CH_3COOH $K_a = 10^{-pK_a} = 10^{-4.76}$ $[CH_3COOH]_0 = 0.500\,\mathrm{mol\,dm^{-3}}$
5.	Plug the two known values into the expression and use the GDC intersect function to calculate the unknown	$K_a = \dfrac{x^2}{[CH_3COOH]_0 - x}$ $10^{-4.76} = \dfrac{x^2}{0.5 - x}$ GDC plot $f_1(x) = 10^{-4.76}$ and $f_2(x) = \dfrac{x^2}{0.5 - x}$ GDC intersect gives: $x = 2.9 \times 10^{-3}\,\mathrm{mol\,dm^{-3}} = [H_3O^+]$
6.	Answer the question (by using the pH formulas)	$pH = -\log[H_3O^+]$ $= -\log 2.9 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ $= 2.53$

8.5 Buffers

Buffer a buffer solution resists changes in pHwhen relatively small amounts of acid or base are added

Buffer composition a solution containing a weak acid with its conjugate weak base in approximately equal amounts

pH of a buffer approximately equal to the $pK_a$of the weak acid

Acidic buffers	**Alkaline buffers**
all (halogenated) carboxylic acids	all amines incl. NH_3

To prepare a solution with the buffer composition we can mix:

1. a weak acid + its conjugate weak base (approx. equal amounts)
2. a weak acid in excess + strong base
3. a strong acid + weak base in excess

When a strong acid or base is added to a weak base or acid, first a completion reaction occurs. When this reaction completes, *the resulting solution* will have the buffer composition: weak acid + its conjugate weak base.

For example, a buffer solution forms when 2.0 mol HA *(excess weak acid)* is mixed with a solution containing 1.0 mol NaOH *(limiting strong base)*. The result of the completion reaction is a solution with equal amounts of weak acid + conjugate weak base (= buffer):

	HA	$+$	$NaOH$	$\longrightarrow$	A^-	$+$	Na^+	$+$	H_2O
before reaction	2.0 mol		1.0 mol		0 mol		–		–
after reaction	1.0 mol		0 mol		1.0 mol		–		–

8.6 pH curves

Titration analytical method to accurately determine the concentration of a substance (analyte), by reference to a known standard solution (titrant)

Analyte substance under investigation, unknown concentration

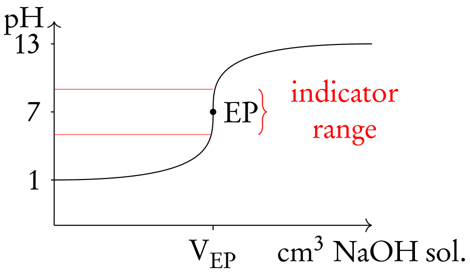
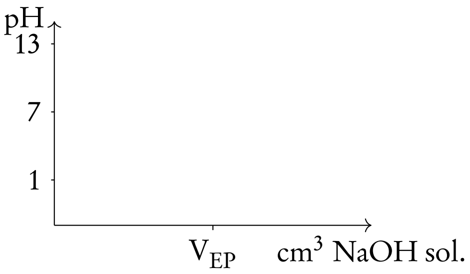
Titrant substance that reacts with the analyte, with known concentration

Equivalence point (EP) where the amount of analyte equals the amount of titrant. Indicators show when the equivalence point is reached.

In acid/base titrations, the concentration of an acid in solution can be determined, by reference to a known base solution, and vice versa.

The acid/base reaction that occurs must be a completion reaction, otherwise the equivalence point cannot be accurately determined. This means that one at least one component in the titration has to be strong, or both. How the pH changes during a titration can be visualised in pH curves.

There are two possible situations: 1. both the analyte and titrant are strong, or 2. one is strong and the other weak. Below, two examples are given for both situations.

	1. strong acid + strong base	2. weak acid + strong base
Analyte	HCl	CH_3COOH
Titrant	NaOH	NaOH
Reaction	$HCl + NaOH \longrightarrow NaCl + H_2O$	$CH_3COOH + NaOH \longrightarrow NaCH_3COO + H_2O$
pH curves		
EP	when amount HCl = amount NaOH, in other words when $[H_3O^+] = [OH-]$, which is neutral so pH = 7 at EP	when amount CH_3COOH = amount NaOH, during titration $NaCH_3COO$ forms, which is alkaline so pH > 7 at EP
Indicator	bromophenol blue	phenolphthalein
Characteristic features		At $\frac{1}{2}V_{EP}$, the amount of NaOHadded = $\frac{1}{2}CH_3COOH$ present. At this point half the weak acid is converted into its conjugate base and forms a buffer. At $\frac{1}{2}V_{EP}$, $pH = pK_a$

8.7 Acid Deposition

Acid deposition acidic particles leave the atmosphere. 2 types: wet (acid rain) and dry (gaseous deposition)

Regular rainwater naturally acidic ($pH = 5.6$) due to the presence of dissolved CO_2

Acid rain made more acidic by SO_x and NO_x (fog, dew, snow, rain)

Sources of SO_x

- Volcanoes
- Combustion of S containing fossil fuels (coal, diesel, ...):

$$S + O_2 \longrightarrow SO_2$$

Formation of SO_3

$$2SO_2 + O_2 \rightleftharpoons SO_3$$

Wet deposition

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \quad \text{(weak acid)}$$
$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \quad \text{(strong acid)}$$

Sources of NO_x

- Electrical storms & bacteria
- Any combustion engine (air at high temperature and pressure):

$$N_2 + O_2 \rightleftharpoons 2NO$$

Formation of NO_2

$$2NO + O_2 \rightleftharpoons 2NO_2$$

Wet deposition

$$2NO_2 + O_2 \longrightarrow \underset{\text{weak}}{HNO_2} + \underset{\text{strong}}{HNO_3}$$

Environmental effects

Acid rain triggers a number of inorganic and biochemical reactions with deleterious environmental effects. To counteract its effects we should 1. Switch to alternative methods of energy production (not fossil fuels) and use less energy (e.g., public transport, reduce consumption). And 2. reduce SO_x and NO_x production by cleaning exhaust gases using catalytic converters and removing S before, during and after combustion (scrubbing).

Vegetation The soil quality degrades because: 1. nutrients (Mg^{2+}, Ca^{2+}, ...) are leached (removed) leading to less chlorophyll production and stunted growth in plants and 2. poisonous Al^{3+} ions are discharged by chemical erosion of rocks, which damages the roots preventing the plants to take up water.

Lakes & rivers Acids damage mucous membranes, making aquatic life (fish, snails, insect larvae, algae) very sensitive to pH. Lime CaO / $Ca(OH)_2$ is sometimes added to lakes to neutralise acidity. Additionally, the poisonous Al^{3+} ions that is discharged by chemical erosion of rocks is poisonous to fish.

Human health Acids also damage human mucous membranes, causing respiratory ilnesses such as asthma, bronchitis, ...

Buildings & structures Marble and limestone consists of the insoluble $CaCO_3$, and the carbonate is a base which reacts with acid to form CO_2 and soluble compounds: $CaCO_3 + H_3O^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$. Metals like steel, bronze, copper, and iron are also corroded by acid rain.

REDOX

9

9.1 Oxidation states

Oxidation is loss of electrons, the reducing agent loses electrons.

$Mg \longrightarrow Mg^{2+} + 2e^-$ Mg is oxidized (loss of e^-), the oxidation state increases.

Reduction is gain of electrons, the oxidising agent gains electrons.

$O_2 + 4e^- \longrightarrow 2O^{2-}$ O_2 is reduced (gain of e^-), the oxidation state decreases.

Since electrons are transferred in a redox reaction, this implies that the charges should change. But it's not always so obvious...

Oxidation state hypothetical charge that an atom would have, if all bonds between different elements were 100% ionic (no covalent component).

Redox reaction reaction between an oxidising and a reducing agent, characterised by the transfer of electrons. In *all* redox reactions, the oxidation state of at least one atom changes.

To help you memorize what is what: OIL RIG

Oxidation
Is
Loss of electrons,

Reduction
Is
Gain of electrons

Note that the oxidation state of Mg^{2+} is written as +2, while the charge is written as 2+.

Determine the oxidation state *per atom (!)*

1. The ox. state of ions in an ionic compound are equal to their charge.
2. Elements *not combined with other elements* have ox. number of 0. (e.g. Fe, Cu, H_2, O_2, P_4, S_8, ...)
3. O *when combined* has ox. state of −2 except in peroxides. (e.g. H_2O_2... when it is −1)
4. H *when combined* has ox. state of +1 except in metal hydrides. (e.g. LiH, NaH... when it is −1)
5. The sum of all the ox. states of a species equals the charge.

Example.

What is the oxidation number of…

… Cl in ClO_4^-?

$$\begin{array}{rcl} Cl & = & ? \\ 4\times O & = & -8 \quad + \\ \hline \text{total} & = & 0 \end{array}$$

So the ox. state of Cl is +7.

… C in $H_2C_2O_4$?

$$\begin{array}{rcl} 2\times H & = & +2 \\ 2\times C & = & ? \\ 4\times O & = & -8 \quad + \\ \hline \text{total} & = & 0 \end{array}$$

So the ox. state of C is +3, since the two C atoms have to account for +6.

… P in NaH_2PO_3?

$$\begin{array}{rcl} Na & = & +1 \\ 2\times H & = & +2 \\ P & = & ? \\ 3\times O & = & -6 \quad + \\ \hline \text{total} & = & 0 \end{array}$$

So the ox. state of P is +3.

Students are often flustered that the verb ‘oxidised’ and the noun ‘reducing agent’ belong together. Remember that OIL RIG applies to the verb, but the opposites are used for the nouns ‘species’ / ‘agent’.

Identify which species are oxidised.

From the following reaction, deduce whether Zn is oxidised or reduced:

$$Zn + CuO \longrightarrow Cu + ZnO$$

1.	Is the element losing or gaining electrons?	ZnO is an ionic compound with zinc present as Zn^{2+}. The Zn metal *loses* two electrons to form the Zn^{2+} ion.
2.	Apply ‘OIL RIG’	Oxidation is loss, so Zn metal is oxidised.

Identify which species is the oxidising or reducing agent.

From the following reaction, deduce whether Cu^{2+} is the oxidising or reducing agent:

$$Cu^{2+} + Mg \longrightarrow Cu + Mg^{2+}$$

1.	Is the element losing or gaining electrons?	The Cu^{2+} ion *gains* two electrons to form the Cu metal.
2.	Apply ‘OIL RIG’	Reduction is gain, so Cu^{2+} is reduced.
3.	Reducing agents are oxidised, and oxidising agents are reduced	Cu^{2+} is an oxidising agent.

9.2 Reactions

The overall balanced redox reaction can be derived from the oxidation and reduction half-reactions. A list of half-reactions can be found in databook table 24: “Standard electrode potentials at 298 K”.

Half-reactions are used to seperate the oxidation and reduction parts of a redox reaction, useful as a tool to balance redox reactions.

Balance redox reactions from the half-reactions.

An acidified potassium permanganate solution reacts with a copper coin. Write down the balanced redox reaction from the half-reactions.

1.	Find both half-equations (DB 24).	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \vert \times 2$ $Cu \longrightarrow Cu^{2+} + 2e^- \quad \vert \times 5$
2.	Balance e^- by multiplying both half-reactions.	$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 5Mn^{2+} + 20H_2O$ $5Cu \longrightarrow 5Cu^{2+} + 10e^-$
3.	Add both half-reactions.	$2MnO_4^- + 16H^+ + 10e^- + 5Cu \longrightarrow$ $2Mn^{2+} + 8H_2O + 5Cu^{2+} + 10e^-$
4.	Cross out the same particles on both sides.	$2MnO_4^- + 16H^+ + \cancel{10e^-} + 5Cu \longrightarrow$ $2Mn^{2+} + 8H_2O + 5Cu^{2+} + \cancel{10e^-}$

Create a half-reaction when reactant and product are known.

Complete the following half-reaction: $N_2H_4 \longrightarrow NO_3^-$

1.	Balance elements other than O and H	$N_2H_4 \longrightarrow 2NO_3^-$
2.	Balance O by adding H_2O	$N_2H_4 + 6H_2O \longrightarrow 2NO_3^-$
3.	Balance H by adding H^+	$N_2H_4 + 6H_2O \longrightarrow 2NO_3^- + 12H^+$
4.	Balance charge by adding e^-	$N_2H_4 + 6H_2O \longrightarrow 2NO_3^- + 12H^+ + 10e^-$

9.3 Reactivity

Standard conditions ($^\ominus$) all dissolved particles have $[\ldots] = 1\,\text{mol}\,\text{dm}^{-3}$, $P = 100\,\text{kPa}$ and $T = 298\,\text{K}$.

Standard hydrogen electrode (SHE) is the reference point with which the electrode potentials of other half-reactions are measured and compared. The standard electrode potential of the SHE is arbitrarily assigned a value of 0 V under standard conditions.

Standard electrode potential $E^\ominus$ the potential difference of a reversible half-reaction under standard conditions, measured against the standard hydrogen electrode.

The standard electrode potential is a measure for the tendency of a substance to react as an oxidising or reducing agent. Metals tend to form cations, so metals tend to lose electrons (metals are oxidised). Non-metals tend to form anions, so non-metals have to gain electrons (non-metals are reduced).

DB 24 shows an ordered list of oxidising agents and reducing agents with their corresponding $E^\ominus$. The strongest oxidising agent is F_2 (it is the most electronegative, so we may expect it to attract electrons), and the strongest reducing agent is Li.

Activity series of metals

The activity series ranks metals according to their reduction potential. Noble metals resist oxidation, so the less noble a metal is the more readily it oxidises. So Au resists oxidation, while Li promotes oxidation. The activity of metals is shown in DB 25. Note the position of H: metals below H do not oxidise in an acidic solution.

Li metal will react with other metal cations, since it is such a strong reducing agent. The more (re)active metal will donate e^- to the lesser active metal.

Determine the order of activity from a set of reactions.

What is the correct order of reactivity of the metals X, Y and Z based on the following equations?

1. $XCl + Y \longrightarrow YCl + X$
2. $ZCl + X \longrightarrow XCl + Z$

1.	The more (re)active metal donates e^-.	1. Y donates electrons, so Y > X 2. X donates electrons, so X > Z
2.	Combine the activities in an ordered list	Y is more reactive than X is more reactive than Z

9.4 The Winkler Method and calculating the Biological Demand (BOD)

BOD is dissolved oxygen in water which can be calculated using redox titrations: **The Winkler Method.**
We calculate the level of BOD in water to gain insight into the healthiness of the water system.
As the level of pollution in the water increases, the dissolved oxygen content decreases- the oxygen is used by bacteria in decomposition reactions.
A low level of BOD is a result of **Eutrophication.**

BOD:
The amount of Oxygen used to decompose the organic matter in a sample of water over a specified time period .

The principle is based on the following sequence of redox reactions:

1. $2\,\underset{+2}{\mathrm{Mn}}^{2+}\,(aq) + O_2\,(g) + 4\,OH^-\,(aq) \longrightarrow 2\,\underset{+4}{\mathrm{Mn}}O_2\,(s) + 2\,H_2O\,(l)$
   - The dissolved Oxygen is fixed by the addition of a Magnese (II) salt.
   - Reaction of O_2 in basic solution causes oxidation of Mn(II) ⟶ Mn(IV)

2. $\underset{+4}{\mathrm{Mn}}O_2\,(s) + 2\,I^-\,(aq) + 4\,H^+\,(aq) \longrightarrow \underset{+2}{\mathrm{Mn}}^{2+}\,(aq) + I_2\,(aq) + 2\,H_2O\,(l)$
   - Acidified iodide ions are added to the solution
   - $I^- \longrightarrow I_2$

3. $2\,S_2O_3{}^{2-}\,(aq) + I_2\,(aq) \longrightarrow 2\,I^-\,(aq) + S_4O_6{}^{2-}\,(aq)$
   - The iodine produced is titrated with sodium thiosulfate

9.5 Electrochemical cells

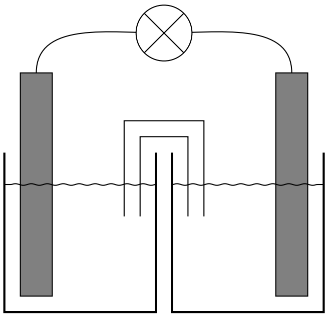
Half-cell consists of a (metal) conductor in contact with an aqueous solution which contains ions. They are used to *physically* separate the red. & ox. half-reactions, and to force the electrons through an external circuit.

Voltaic cell converts chemical energy from spontaneous, exothermic chemical reactions to electrical energy.

AN OIL RIG CAT:
ANode is the electrode where
Oxidation
Is
Loss of electrons, and
Reduction
Is
Gain of electrons at the
CAThode.

Components of a voltaic cell:

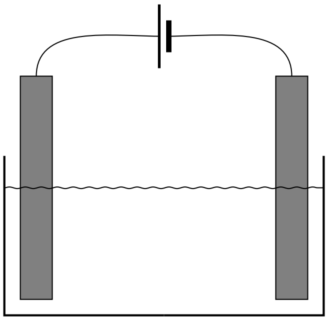
- Separated halfcells
- Conducting electrodes
- Electrolyte solutions
- Salt-bridge
- External circuit



Electrolytic cell converts electrical energy to chemical energy, by bringing about non-spontaneous chemical reactions.

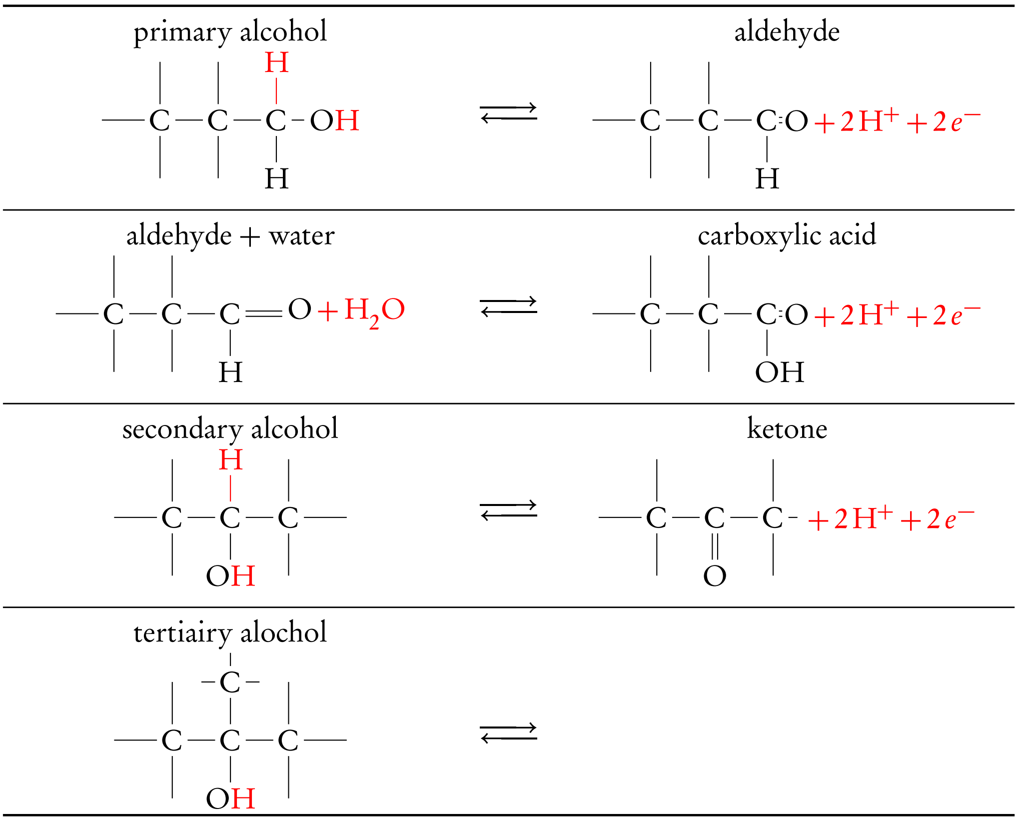
Components of an electrolytic cell:

- Single cell possible
- Conducting electrodes
- Electrolyte solutions
- External power source



		Voltaic cell	Electrolytic cell
Anode	oxidation occurs here	circle –	circle +
Cathode	reduction occurs here	circle +	circle –

9.6 Oxidation of alcohols



ORGANIC CHEMISTRY

10

10.1 Fundamentals of organic chemistry

Organic chemistry is the field of chemistry that studies carbon-based compounds. Carbon can form bonds with neighbouring atoms using its four valence electrons, and is capable of catenation – the process of many identical atoms connecting bonding covalently to produce long straight or branched chains or cyclical structures. Carbon

A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit.

Members of a homologous series have similar chemical properties and they show a gradual change in physical properties. The gradation in physical properties occurs with the increase of length of the carbon chain. For example, the boiling and melting points generally increase as we progress in the homologous series as a result of increasingly strong intermolecular forces.

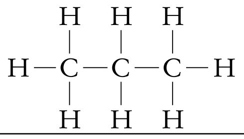
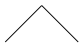
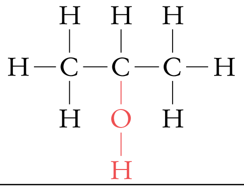
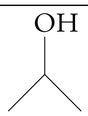
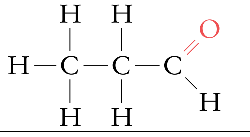
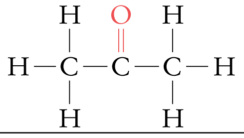
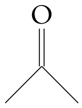
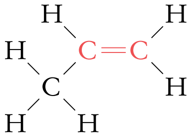
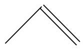
10.1.1 Chemical formulae of organic compounds

A distinction should be made between empirical, molecular and different types of structural formulas for organic compounds.

Empirical formulae the simplest ratio of atoms present in a molecule.
Molecular formulae the actual number of atoms present in the molecule.
Structural formulas can be full, condensed or skeletal.
- **Full** structural formula – two-dimensional representation showing all atoms and bonds and their relative arrangements in the compound.
- **Condensed** structural formula – all atoms and their relative positions are represented but the bonds between them are omitted.
- **Skeletal** structural formula – the most basic representation of the structural formulas where carbons and hydrogens are omitted. The atoms in the functional group are present in the skeletal formula.

Table 10.1 below shows the difference between the different structural formulae:

Table 10.1

Name	Full structural formula	Condensed structural formula	Skeletal formula
propane		$CH_3CH_2CH_3$	
propan-2-ol		$CH_3CH(OH)CH_2$	
propanal		CH_3CH_2CHO	
propanone		$CH_3C(O)CH_3$	
propene		$CH_3CH{=}CH_2$ or CH_3CHCH_2	

10.1.2 Nomenclature of organic compounds

Names of organic compounds are given following the standards set out by IUPAC.

Recipe for naming organic compounds:

1. Find the longest continuous carbon chain (table 10.2)
2. If alkyl substituents are present, forming a branched chain, the name of the chain will depend on the number of carbon atoms present in the substituent (see table 10.3)
3. When numbering the chain, the position of any substituents must be the lowest numbered carbon
4. If there are more substituents present arrange them in alphabetical order prior to the root name
5. Use commas to separate numbers
6. Use a hyphen to separate numbers and letters
7. The number of multiple substituents of the same table is given in table 10.4
8. Successive words are merged into one word.

Table 10.2: Prefixes for longest chain

Length of carbon chain	**Name**
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-

Table 10.3: Names for substituents

Substituent name	**Condensed formula**
methyl	$-CH$
ethyl	$-CH_2Ch_3$
propyl	$-CH_2Ch_2Ch_3$
butyl	$-CH_2CH_2CH_2CH_3$

Table 10.4: Prefixes for multiple same substituents

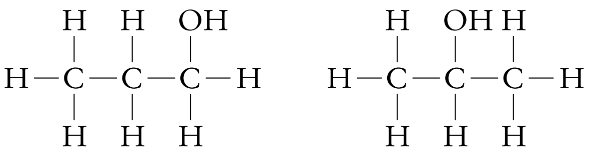
1	mono
2	di
3	tri
4	tetra
5	penta

It is important to be able to derive the structural formula correctly from its name as it is necessary to distinguish between compounds which might share their molecular formula.

Structural isomers are compounds with the same molecular formula but different arrangements of atoms.

An example of structural isomerism is shown in figure 10.1. Both compounds have the molecular formula C_3H_7OH but the position of the OH group is different.

Figure 10.1: Structural isomerism of C_3H_7OH



propane-1-ol

propane-2-ol

10.1.3 Saturated and unsaturated hydrocarbons

Hydrocarbons are compounds containing only hydrogen and carbon atoms.

Saturated hydrocarbons contain only single carbon-carbon bonds.

Unsaturated hydrocarbons contain double and/or triple carbon-carbon bonds.

Aliphatic compounds compounds whose carbons are linked in open chains, either straight or branched (without benzene rings).

Aromatic compounds compounds containing at least one benzene ring.

10.1.4 Functional groups

Functional groups are the reactive part of the molecule. These commonly contain elements such as oxygen or nitrogen.

Compounds can either be synthetic (made from natural and man-made compounds) or natural (synthesized by organisms). Different compounds that all contain the same functional group are divided into classes, sometimes the name of the class is the same as the functional group, while other times it is different. For example, the name of the class is the same for all esters which contain the ester functional group (—COOR) but it is different for all alcohols that contain the hydroxyl (—OH) functional group.

When naming compounds with a functional group the position of the functional group is denoted by giving the number of the carbon atom it is attached to and when numbering the carbon atoms the functional group has priority over any substituents and carbon-carbon multiple bonds.

Tables 10.5 and 10.6 provide an overview of a number of important functional groups.

Table 10.5

Atom or grouping	Name
—CL	chlorine atom
—F, —Cl, —Br, —I	halide 'group'
—OH	alcohol group
—CHO	aldehyde group
—COOH	carboxylic acid group
—NH$_2$	amine group
—CONH$_2$	amide group
—CN	nitrile group

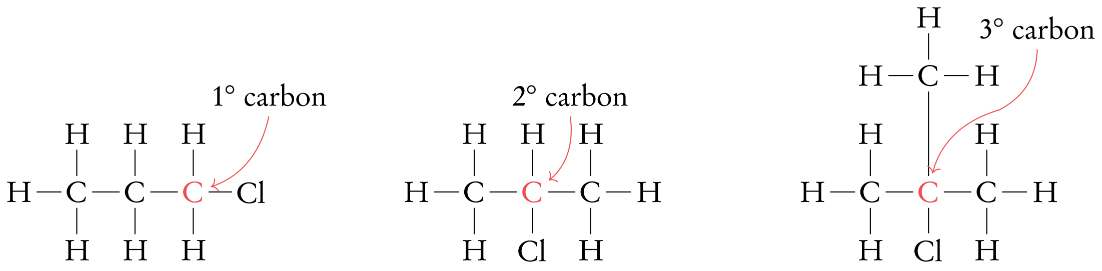
Table 10.6

Linking atom or group	Name
—O—	ether link
—COO—	ester link
—NHCO—	amide link
—O—O—	peroxide link

10.1.5 Classifying molecules: primary, secondary, tetriary compounds

A primary carbon is attached to only one other carbon.
A secondary carbon is attached to two other carbon atoms.
A tetriary carbon is attached to three other carbon atoms.

Figure 10.2: Halogenoalkanes

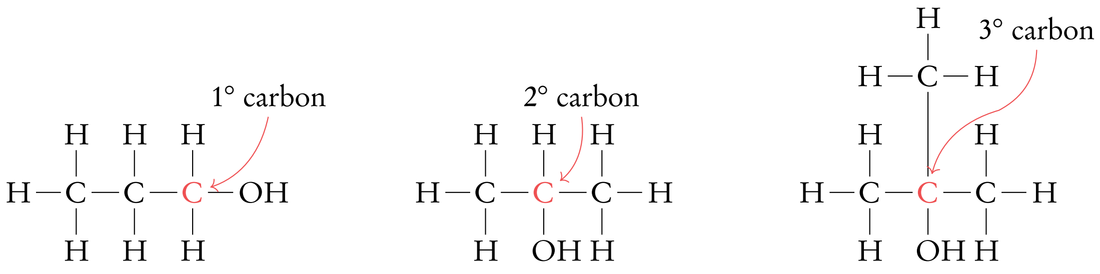


1-chloropropane

2-chloropropane

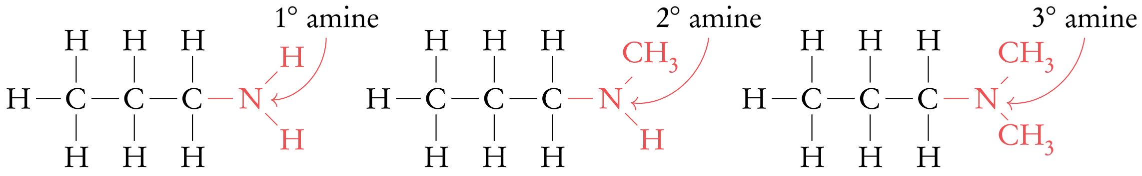
2-chloro-2-methylpropane

Figure 10.3: Alcohols



propan-1-ol propan-2-ol 2-methylpropan-2-ol

Figure 10.4: Amines



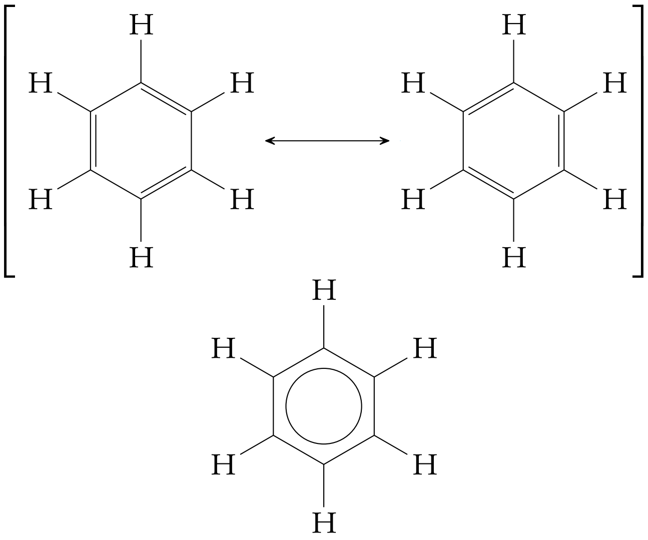
propan-1-amine N-methylpropan-1-amine N,N-dimethylpropan-1-amine

10.1.6 Aromatic hydrocarbons

Compounds characterised by the presence of a benzene ring.

Benzene (molecular formula C_6H_6) has a ring-like structure, with each carbon bonded to two other carbons and a hydrogen atom. While it was initially thought that benzene contained alternating single and double bonds it has been experimentally confirmed that all carbon-carbon bonds are of the same length (between the length of a single and double bond). Each carbon in beznene is sp^2 hybridized and bonded to two other carbons and a hydrogen atom. The six p orbitals of the sp^2 hybridized carbons overlap with each other and form a continuous π bond that lies above and below the plane of the six carbon atoms. We denote the delocalisation of the π bond using resonance structures shown below to represent benzene.

Figure 10.5



The delocalisation of p electrons gives benzene additional stability. As a result benzene readily undergoes electrophilic substitution reactions but does not generally show addition reactions as other unsaturated aliphatic and cyclic compounds.

10.2 Functional group chemistry

Common reactions studied in organic chemistry include substitution, addition and elimination. Substitution is the replacement of individual atoms with other single atoms or a small group of atoms. In an addition two molecules are added together to produce a single molecule. Elimination is the removal of two substituents from the molecule.

10.2.1 Alkanes

- Simplest hydrocarbons
- Low bond polarity and strong carbon-carbon and carbon-hydrogen bonds, hence relatively inert (unreactive)
- Important reactions we consider and halogenation

Combustion reactions

- Alkanes are often used as fuels
- As the length of the chain increases the volatility decreases (tendency to change state from liquid to gas)
- Alkanes undergo complete combustion in excess oxygen (see example for propane)

$$C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O$$

Halogenation reactions

Alkanes can undergo free-radical substitution and elimination to form alkenes or alkyls

Free radical substitution

We consider a reaction between methane and chlorine in the presence of UV light as an example of free-radical substitution. The reaction proceeds in several stages which are outlined below.

Two chlorine radicals are formed in the process of homolytic fission.

Homolytic fission splitting of a covalent bond whereby the two atoms get one electron each from the covalent bond.

Free radicals reactive species formed when a molecule undergoes homolytic fission.

The reaction occurs in three stages: initiation, propagation and termination.

1. Initiation

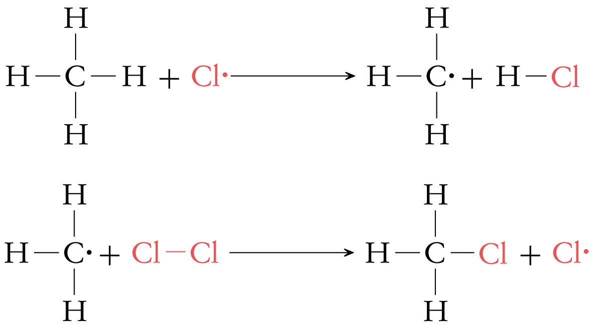
The bond in Cl_2 is broken by homolytic fission in the presence of UV light and two free radicals are produced from one chlorine molecule.

$$Cl-Cl \xrightarrow{UV} Cl\cdot + Cl\cdot$$

2. Propagation

The free radicals will react with the molecules present in solution and as a result produce new free radicals which then continue reacting with other molecules. Note that the two reactions are examples of propagation reactions, there are other possible reactions as well.

In the exam you will typically be asked to write 2 or 3 reactions for the propagation stage.

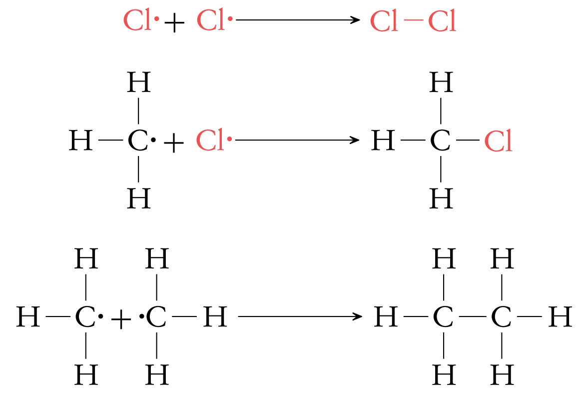


$$CH_4 + Cl\cdot \longrightarrow CH_3\cdot + H-Cl$$

$$CH_3\cdot + Cl-Cl \longrightarrow CH_3-Cl + Cl\cdot$$

3. Termination

A termination step reduces the concentration of radicals in the reaction mixture. The radicals recombine to form new molecules.

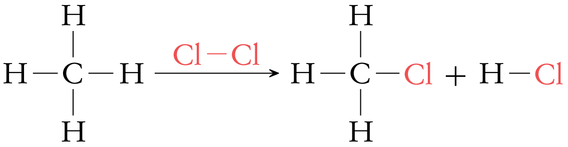


$$Cl\cdot + Cl\cdot \longrightarrow Cl-Cl$$

$$CH_3\cdot + Cl\cdot \longrightarrow CH_3-Cl$$

$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3-CH_3$$

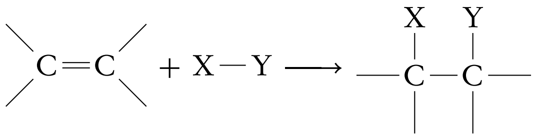
The net reaction can be written down as follows:



$$CH_4 \xrightarrow{Cl-Cl} CH_3-Cl + H-Cl$$

10.2.2 Alkenes

Due to the presence of at least one double carbon-carbon bond alkenes are more reactive than alkanes. The most important reactions of alkenes are addition reactions. Reactive molecules are able to add across the double bond. The reacting alkene is said to be unsaturated because of the double bond while the product is said to be saturated (contains only single carbon-carbon bonds).



unsaturated saturated

Addition reactions include the addition of hydrogen, bromine, hydrogen halides and water.

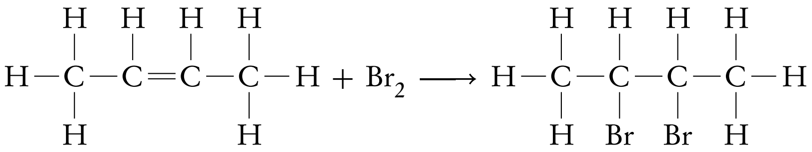
Hydrogenation

We use the example of ethene here, but the same reaction holds for alkenes in general. In the presence of finely divided nickel catalyst at a temperature of 150°C, ethene will undergo an addition reaction with hydrogen gas to produce the saturated alkane ethane:

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow[\Delta]{Ni} C_2H_{6(g)}$$

Halogenation

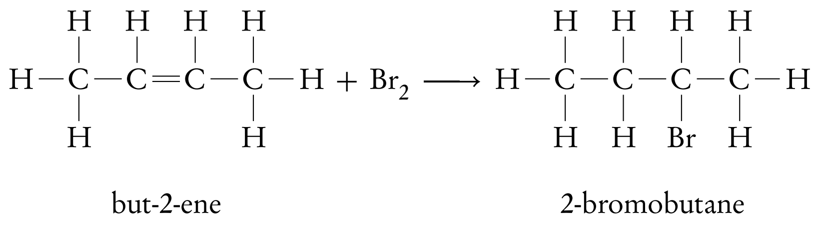
The electrophilic halogenation of symmetrical alkenes involves the addition of elemental halogens (e.g. Cl_2, Br_2) to produce dihalogenated alkanes.



$$\begin{array}{ccccccccccccccccccccccc}
& & H & & H & & H & & H & & & & & & & H & & H & & H & & H & \\
& & | & & | & & | & & | & & & & & & & | & & | & & | & & | & \\
H & - & C & - & C & = & C & - & C & - & H & +\,Br_2 & \longrightarrow & H & - & C & - & C & - & C & - & C & - & H \\
& & | & & & & & & | & & & & & & & | & & | & & | & & | & \\
& & H & & & & & & H & & & & & & & H & & Br & & Br & & H &
\end{array}$$

but-2-ene 2,3-dibromobutane

The addition of hydrogen halide, HX, to a symmetrical alkene results in a mono-halogenated alkane. With unsymmetrical alkenes two products are possible (this is covered in HL content).



Reacting ethene with steam in the presence of a catalyst (phosphoric(V) acid) results in the production of ethanol.

$$C_2H_{(4g)} + H_2O_{(g)} \longrightarrow C_2H_5OH_{(g)}$$

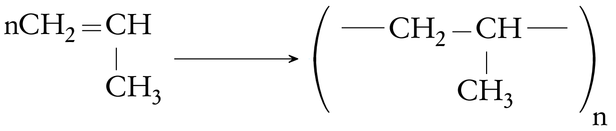
Polymerization

Polymerization the reaction of many monomers containing a double bond linking together to form a polymer

Alkenes can undergo addition polymerization. The ethene polymer undergoes addition polymerization to produce polyethene.

$$nC_2H_4 \longrightarrow [-CH_2-CH_2-]_n$$

The repeating structural unit of the polymer reflects the structure of the monomer, with double bond replaced by a single bond and the electrons form the double bond donated to the adjacent carbon. For example, the polymerization of propene is represented as follows:



$$n\underset{\displaystyle CH_3}{\overset{}{CH_2=\underset{|}{CH}}} \longrightarrow \left(-CH_2-\underset{\displaystyle \overset{|}{CH_3}}{CH}- \right)_n$$

Note: Both alcohols and alkenes can also undergo complete combustion reactions but here we focus on their most important reactions.

10.2.3 Alcohols

Alcohols undergo nucleophilic substitution reactions with acids (also called esterification or condensation) and some undergo oxidation reactions.

Oxidation of alcohols

Acidified potassium dichromate(VI) or potassium manganate(VII) can be used for the oxidation of alcohols.

The oxidation products of alcohols depend on the type of alcohols involved.

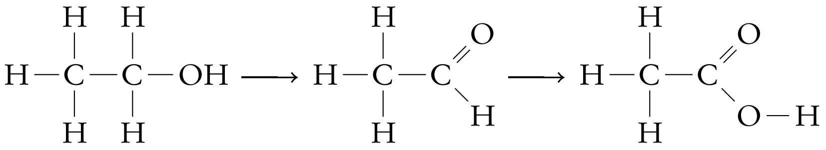
$$\mathrm{MnO}^{-}_{4(\mathrm{aq})} + 8\,\mathrm{H}^{+}_{(\mathrm{aq})} + 5\,\mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+}_{(\mathrm{aq})} + 4\,\mathrm{H_2O}_{(\mathrm{l})}$$

$$\mathrm{Cr_2O}^{2-}_{7(\mathrm{aq})} + 14\,\mathrm{H}^{+}_{(\mathrm{aq})} + 6\,\mathrm{e}^{-} \longrightarrow 2\,\mathrm{Cr}^{3+}_{(\mathrm{aq})} + 7\,\mathrm{H_2O}_{(\mathrm{l})}$$

Primary alcohols

The oxidation of primary alcohols is a two-stage process that first produces an aldehyde followed by a carboxylic acid.

When a primary alcohol, ethanol, is heated with acidified potassium dichromate, the aldehyde ethanal is produced. This aldehyde can be further oxidized to the carboxylic acid ethanoic acid.



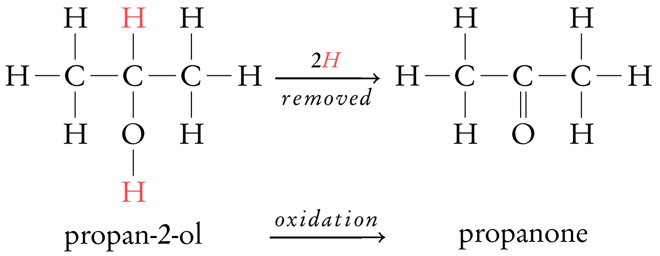
ethanol ethanal ethanoic acid

The aldehyde can be recovered by the process of distillation, preventing its further oxidation. This is possible because the aldehyde has a lower boiling point than the carboxylic acid due to the presence of weaker intermolecular forces (IMFs): aldehydes have weak dipole-dipole IMFs while carboxylic acids have stronger intermolecular hydrogen bonds and so have higher boiling points.

If the carboxylic acid is the desired product, the aldehyde must remain in the reaction mixture with the oxidizing agent for a longer period of time and reflux column is used. Refluxing is a technique that involves cyclic evaporation and condensation of a volatile reaction mixture, preserving the solvent as it does not evaporate.

Secondary alcohols

When a secondary alcohol is oxidised the product is a ketone and no further oxidation is possible.



Tetriary alcohols cannot be oxidized.

10.2.4 Condensation reaction of an alcohol and a carboxylic acid

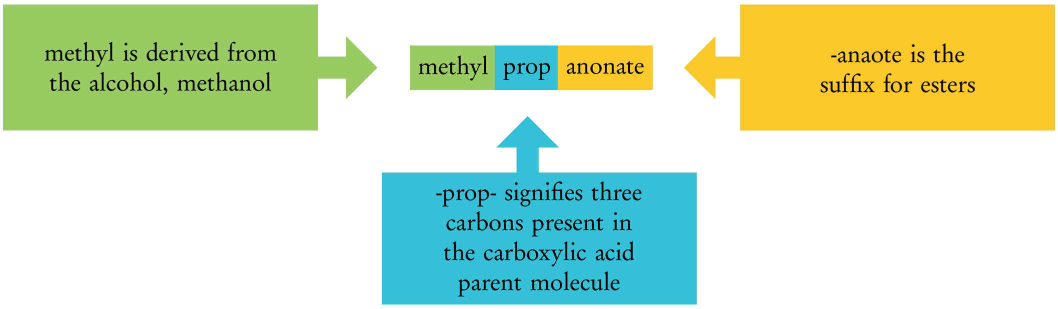
Esterification is a reversible reaction that occurs when a carboxylic acid and an alcohol are heated in the presence of a catalyst, usually concentrated sulfuric acid.

$$CH_3CH_2COOH_{(l)} + CH_3OH_{(l)} \xrightarrow{H_2SO_{4(conc)}} CH_3CH_2COOCH_{3(l)} + H_2O_{(l)}$$

propanoic acid methanol methyl propanoate

Figure 10.6 below summarizes naming esters.

Figure 10.6


methyl is derived from the alcohol, methanol

methyl prop anonate

-anaote is the suffix for esters

-prop- signifies three carbons present in the carboxylic acid parent molecule

10.3 Types of organic reactions

10.3.1 Nucleophilic substitution reactions

Halogenoalkanes are more reactive than alkanes due to the presence of the very electronegative halogen and hence the polar carbon-halogen bond. The partial positive charge on the carbon makes the carbon electron deficient, and hence susceptible to attacks by nucleophiles – electron rich species capable of donating a pair of electrons to form a covalent bond.

The mechanisms for nucleophilic substitution (S_N) depends on the type of halogenoalkane involved.

10.3.2 S_N2 reactions and primary halogenoalkanes

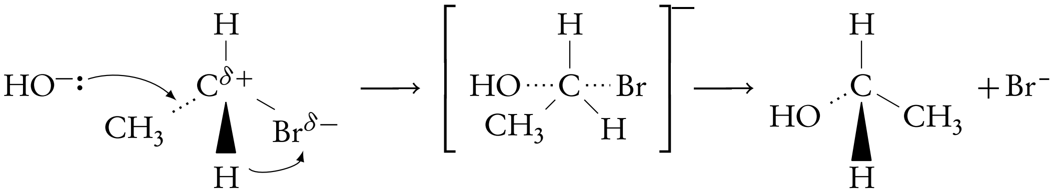
Nucleophilic substitution in primary halogenoalkanes proceeds in one step. Both the halogenoalkane and the nuclephile are present in the rate-determining step (slow step) so the rate of reaction depends on concentrations of both reactants. Hence, this is described as a second order reaction and we can express the rate as follows:

$$\text{Rate} = k[\text{halogenoalkane}][\text{nucleophile}]$$

The molecularity of this reaction is described as bimolecular.

An example is a reaction between bromoethane and aqueous hydroxide ion, which yields ethanol and the bromide leaving group.

Figure 10.7



The partially positively charged carbon atom is attacked by the hydroxide nucleophile, forming a transition state that involves both the halogenoalkane and the nucleophile. The transition state features a partially formed covalent bond between the carbon atom and the nucleophile, and a weakened carbon-bromide bond that is still not completely broken.

Notes for drawing S_N2 mechanism

- The curly arrow from tne nucleophile originates from its lone pair or negative charge and terminates at the carbon atom
- The curly arrow representing the bromine leaving group originates at he bond between the carbon and bromine atoms. This can be shown on bromoethane or on the transition state
- Partial bonds are represented by dotted lines in the transition state
- Transition state is enclosed in squared brackets with a single negative charge
- The formation of both the product and the leaving group must be shown

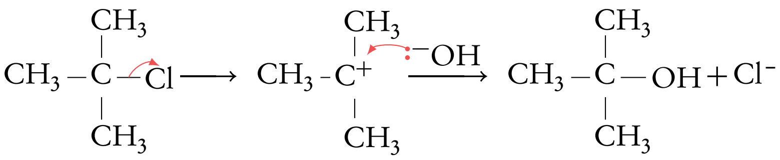
10.3.3 S_N1 reactions and tetriary halogenoalkanes

Tetriary halogenoalkanes undergo nnucleophilic substitution which proceeds in two steps. The rate-determining step involves only the halogenoalkanes the bond to the leaving group breaks, forming a carbocation. The reaction is a first order reaction.

$$\text{Rate} = k[\text{halogenoalkane}]$$

An example of an S_N1 mechanism is the reaction between 2-chloro-2methyl propane and aqueous hydroxide ion.

Figure 10.8



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Cl \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}}\ :^-OH \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH + Cl^-$$

The first step of the reaction is the slow (rate-determining) step and the second step is fast. As there is only one molecule present in the slow step the molecularity of the reaction is unimolecular.

The atoms present in the molecule determine the likely reaction mechanism.

Inductive effects in organic compounds have a significant effect on which nucleophilic substitution mechanism occurs between a nucleophile and a halogenoalkane. The differences in electronegativity between atoms present in the molecule are the most important factor. In the C—H bond the carbon atom has slighly greater electronegativity than hydrogen, which creates a weak dipole and a shift in position of the bonding electrns closer to the carbon atom. Atmos such as more electronegative halogens have a far greater polarizing effect.

Alkyl groups bonded to a carbocation have a positive inductive effect – they stabilize the charged carbocation by donating electron density and reducing the positive charge on the carbocation. In a primary carbocation there is only one alkyl group contributing to the stabilization so it is the least stable one. In a tetriary carbocation there are three alkyl groups attached and contributing to stabilization, hence it is more stable. This is one of the reasons why tetriary halogenoalkanes have a tendency to undergo reactions via the S_N1 mechanism.

Factors affecting the rate of nucleophilic substitution

1. **The nature of the halogen**

   The carbon-halogen bond strength decreases as we move down group 17 and the weaker the bond the more readily it gets broken. Hence, for both S_N1 and S_N2 reactions iodoalkanes react faster than bromoalkanes, which in turn react faster than chloroalkanes.

2. **The nature of the halogenoalkane**

   Tetriary halogenoalkanes react faster than secondary halogenoalkanes, which in turn react faster than primary halogenoalkanes. The S_N1 route which involves the formation of an intermediate carbocation is faster than S_N2 route which involves a transition state.

3. **The choice of solvent**

   S_N2 reactions are best performed in aprotic, polar solvents while S_N1 reactions are carried out in protic, polar solvents.

   Aprotic, polar solvents are suitable for S_N2 because they:
   - Possess no O—H or N—H bond so cannot form hydrogen bonds to the nucleophile
   - Cannot solvate the nucleophile so leaving it "naked" and maintaining its effectiveness as a nucleophile in forming the transition state
   - Examples of such solvents: ethyl ethoanoate ($CH_3COOCH_2CH_3$), propanone ($CH_3C(O)CH_3$)

   Protic, polar solvents are suitable for S_N1 because they:
   - Are polar in nature due to the present of polar bonds
   - Possess either O—H or N—H group so can form hydrogen bonds with the nucleophile
   - Solvate the nucleophile, thus inhibiting its ability to attack electrophiles such as the partially positive carbon atom

Solvation is the process by which solvent molecules surround the dissolved ions.

In general, solvation is more effective for smaller nucleophiles. If the nucleophile is encapsulated by the solvation "shell", it is less effective as a nucleophile in forming an S_N2 intermediate, hence S_N1 reactions are favoured.

Factors which affect the effectiveness of a nucleophile

It is understood that the hydroxid ion is a stronger nucleophile than the water molecule. We use the example of the hydroxide ion and the water molecules to demonstrate factors that influence the strenght of a nucleophile:

- Both nucleophiles possess at least one pair of electrons, so by definition can act as Lewis bases
- The negatively charged hydroxide ion is a stronger nucleophile than water which is its conjugate acid. A negatively charged ion has a far greater attraction for the electrophile than does a neutral molecule

10.3.4 Electrophilic addition reactions

Electrophile electron deficient species that will accept the pair of electrons.

Electrophile can either have a formal positive charge (a cation) or a partial positive charge ($\delta+$) as a result of a polar bond. Examples of electrophiles include NO_2^+, CH_3^+.

When alkenes undergo addition reactions the double bond is broken and a saturated product is formed. Electrophiles can provide the atmos for the two new bonds which are formed in the addition reaction.

A carbon-carbon double bond is an area of high electron density, hence it is susceptible to attacks by electrophiles which are electron deficient. It is important to note the distinction between bond strength and its reactivity – a double bond is stronger than a single and more reactive because of its high electron density.

Markovnikov's rule

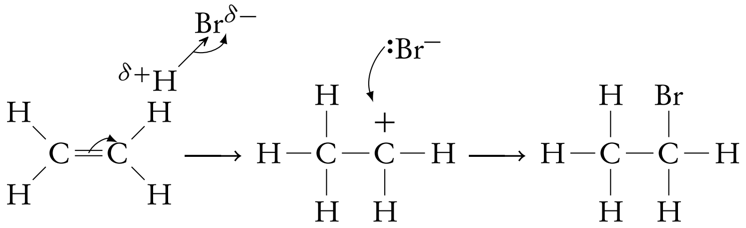
The major products of electrophilic addition of hydrogen halides to unsymmetrical alkenes can be predicted using Markovnikov's rule. According to the rule, the hydrogen atom will preferentially bond to the carbon atom of the alkene that is already bonded to the largest number of hydrogen substituents.

This comes about because the carbocation formed when the π bond is broken has its positive charge centered on the most substituted carbon. A tetriary carbocation has a greater stability than a primary carbocation due to the reduction of density of the positive charge through the inductive effects of the three alkyl substituents.

10.3.5 Addition of hydrogen halides to alkenes

Heterolytic fission breaking of a covalent bond whereby both electrons from the bond go to one of the atoms.

When ethene and hydrogen bromide are reacted, the major product is bromobutate as the hydrogen bromide is split heterolytically, creating the hydrogen cation and the bromide anion. The initial attack on the π electrons in the C=C bond comes from the cation, followed by rapid reaction between the unstable carbocation and the halogen ion.



Notes on drawing mechanisms

- A curly arrow originates from the carbon-carbon double bond to the hydrogen atom of hydrogen bromide
- The curly arrow representing the bromide leaving originates at the bond between the hydrogen and bromide atoms
- A curly arrow goes from the lone pair of the negative charge on Br^- to C^+ (the carbocation)
- The structural formula of the product is shown

Electrophilic addition of halogens to alkenes

The same mechanism as the one previously described is followed when a halogen is added to an alkene. Addint bromine is commonly used as a test for unsaturation.

Electrophilic addition of interhalogens to alkenes

Interhalogens compounds in which two or more halogens are combined in a molecule.

Differences in electronegativity between the halogens will result in an electrophilic region of the molecule and this determines which halogen will attach the π bond.

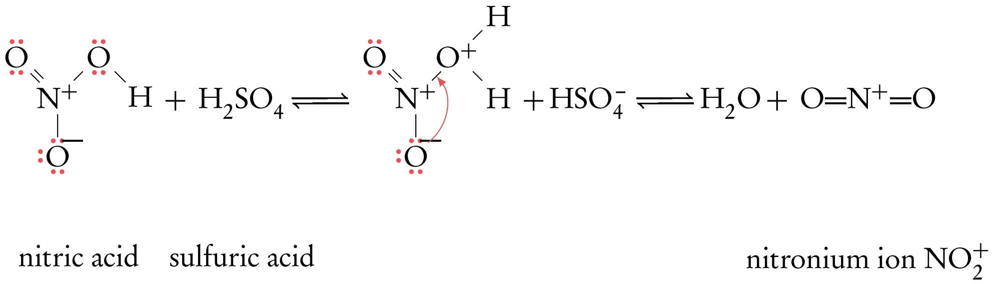
The addition reactions of halogens, halogen halides and interhalogenes to symmetrical alkenes will follow the same mechanisms as the ones for unsymmetrical alkenes. The only difference is that Markovnikov's rule does not apply,

10.3.6 Electrophilic substitution reactions

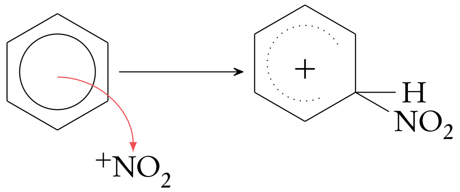
We use the example of the reaction between benzene and the nitronium ion (NO_2^+).

The first step involves the generation of the nitronium ion electrophile. A nitrating mixture of sulfuric acid and nitric acid at 50°C generates a concentration of nitronium ions higher than in the pure nitric acid. This allows the reaction to proceed at an acceptable rate. The reaction is summarized in figure 10.9:

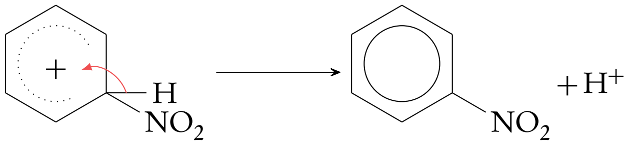
Figure 10.9



As the electrophile (NO_2^+) approaches the delocalized π electrons of the benzene ring, the nitronium ion is attached to the ring. Two electrons from the ring are donated to form a new C—N bond and a π electron from the N=O bond of the nitronium ion moves onto the oxygen atom.



This is the rate-determining step of mechanism, the addition of the nitronium ion to the C=C bond removes the aromaticity of the arene. The water molecule now acts as a base and deprotonates the carbocation in order to restore the aromaticity of the system.



$$C_6H_7 + HNO_3 \xrightarrow[50°C]{H_2SO_4} C_6H_5NO_2 + H_2O$$

The product nitrobenzene is a yellow oil that can be isolated from the reaction mixture.

10.3.7 Reduction of carboxylic acids

Carboxylic acids are first reduced to aldehydes and then eventually to alcohols bu reactions reverse of the oxidation of alcohols we have seen.

Common reducing agents:

- Lithium aluminium hydride, $LiAlH_4$
- Sodium borohydride, $NaBH_4$

The reduction equation is often represented in a simplified manner using [H] to represent the reducing agent. The general equation for the reduction of an aldehyde to a primary alcohol is shown below:

$$R{-}CHO + 2[H] \longrightarrow R{-}CH_2OH$$

The reduction of ketones to secondary alcohols can be represented by the general equation:

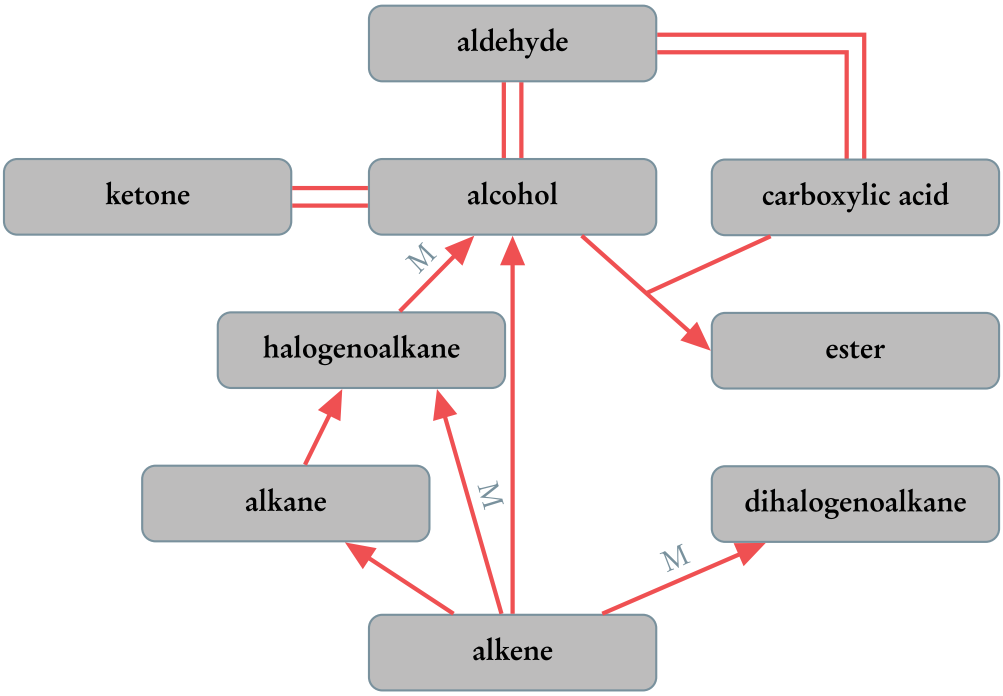
$$R{-}CO{-}R' + 2[H] \longrightarrow R{-}CH(OH){-}R'$$

10.4 Synthetic routes

This sub-topic requires organic synthesis using up to four different steps involving reactions that have already been covered. Rather than looking at the specific compound it is often helpful to look at the functional groups involved and consider the reactions of these groups. For some syntheses it is helpful to work forward from the reactants but it can be equally profitable to work backwards from the product to find the simplest starting materials – a process known as retro-synthesis.

Figure 10.10 below summarizes the pathways you need to be familiar with. The letter M indicates the mechanism is needed for the reaction.

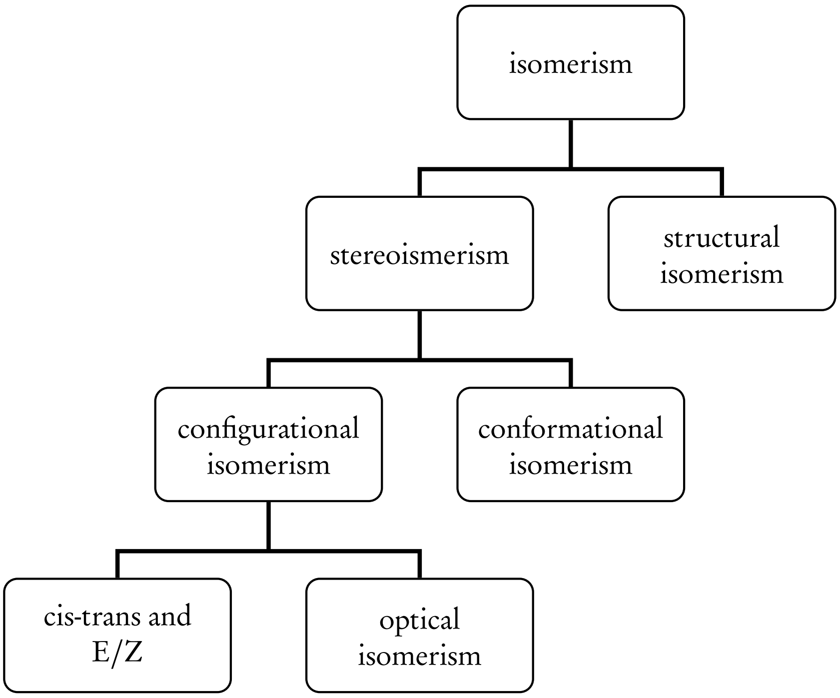
Figure 10.10



10.4.1 Stereoisomerism

We distinguish between several different types of isomerism, which are summarized in figure 10.11 below:

Figure 10.11

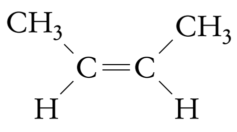


10.4.2 Configurational isomers

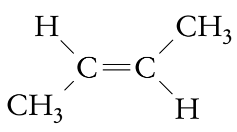
Configurational isomers can only be interconverted by the breaking of bonds or the rearrangement of stereocentres. They are divided into cis-trans and E/Z isomers on the one hand and optical isomers on the other.

Cis-trans isomerism

- Stereoisomers differ from each other in the spatial arrangement of their atoms
- *cis-trans* isomers
- *cis-* same side *trans-* different side
- *cis-trans* prefix written in *italics* before name

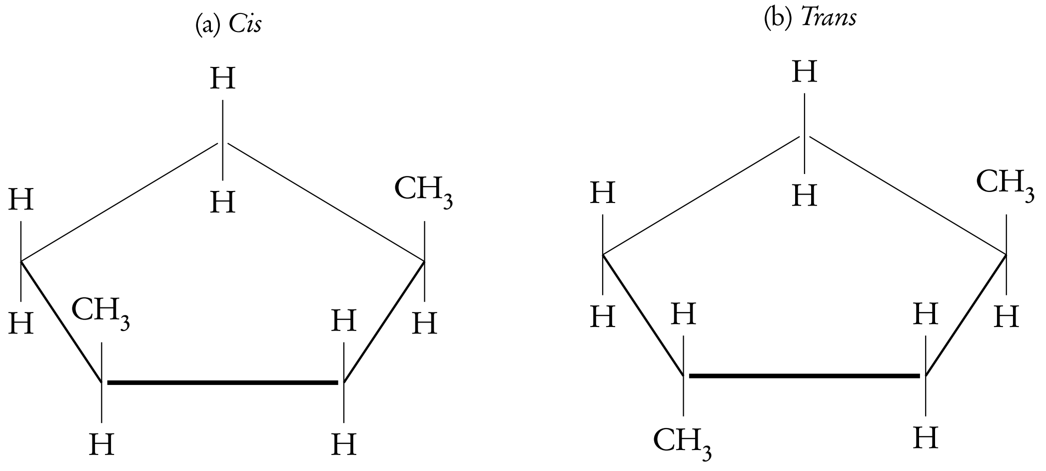


cis-2-butene



trans-2-butene

Figure 10.12



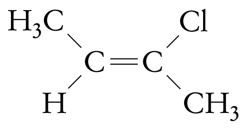
(a) *Cis*

(b) *Trans*

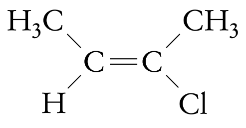
E/Z isomerism

Cis-trans isomerism is a restricted form of E/Z isomerism as it only occurs when two substituents R_1 and R_2 occur on either side of the carbon-carbon double bond. E/Z isomerism covers every case where free rotation around C=C double bond is not possible.

E/Z terminology depends on what are known as the Cahn-Ingold-Prelog (CIP) rules for detemining the priority of the atoms or groups attached to the two carbon atoms of the double bond. Each of the carbon atoms on either side of the double bond is considered separately. Simply put, the higher the atomic number of the attached atoms to each carbon atom – the higher the priority. If the two atoms/groups with the highest priority lie on the same side the isomer is Z and if they lie on the opposite sides the isomer is E. In this simple case Z is the cis- form and E is the trans- form.



trans-2-chlorobut-2-ene
[Z]-2-clorobut-2-ene



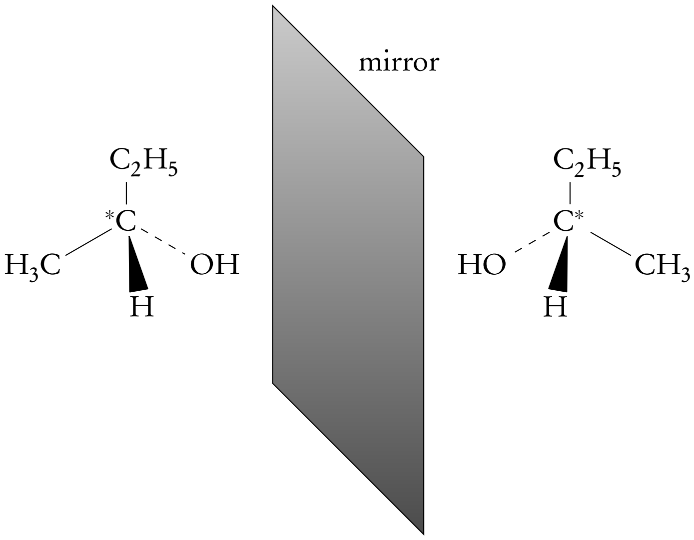
cis-2-chlorobut-2-ene
[E]-2-chlorobut-2-ene

However, Z does not always equate to cis. If you consider 2-chlorobut-2-ene then the carbon atom of the methyl group has priority over the hydrogen atom on one side of the double bond but because chlorine has a higher atomic number than carbon it will have priority over the methyl group on the other side of the double bond. Now the cis-isomer is the E isomer and the trans-isomer is the Z isomer.

10.4.3 Optical isomerism

Optical isomers have an identical arrangement of atoms, but the isomers are mirror images of one another. These mirror images are non-superimposable, just like a pair of gloves. This can only happen if the molecule is asymmetrical. The easiest way for a molecule to be asymmetrical is to have a carbon atom with four different groups or atoms attached. Such an asymmetric carbon atom is called a chiral atom, or centre of chirality.

Mirror image optical isomers are called enantiomers.



Optical isomers and plane polarized light

Optical isomers interact differently with light. A device called a polarimeter is used to distinguish between different optical isomers. In order to test optical isomerism a solution of isomers in a tube is exposed to plane-polarized light and the isomers rotate the light by the same amount but in the opposite direction. The concentration of solution and wavelength of light should be kept the same when performing the analysis. Figure 10.13 below summarizes the process.

Figure 10.13

Physical and chemical properties of optical isomers

Other than rotating plane polarized light optical isomers possess identical physical properties (except in some cases they form asymmetric mirror image crystals).

Optical isomerism is extremely important in biological systems. The chemical properties of optical isomers are identical except when reacting with other optical isomers. Biological systems contain many proteins and complex amino acids, which are optically active. They may be stimulated to react in certain ways by optically active enzymes (biological catalysts).