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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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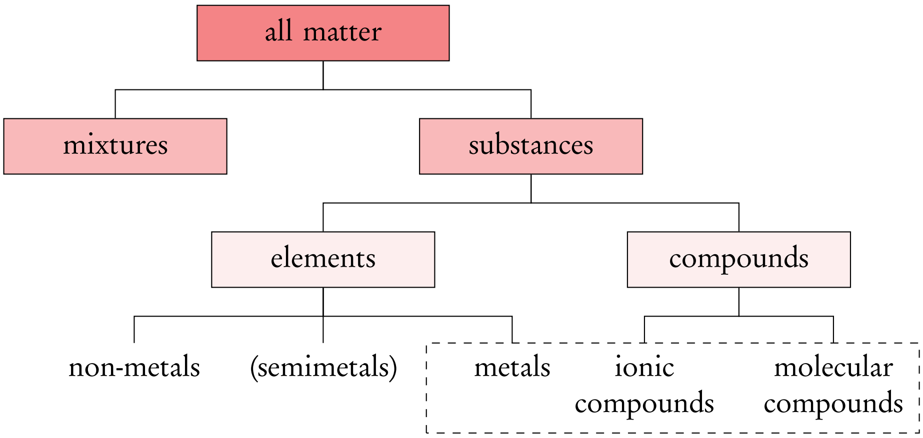
1.1 Types and states of matter



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

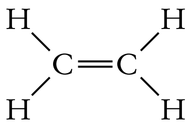
Classification of matter:	type of element(s):
metal	metal
ionic compound	metal + non-metal
molecular compound	non-metal

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

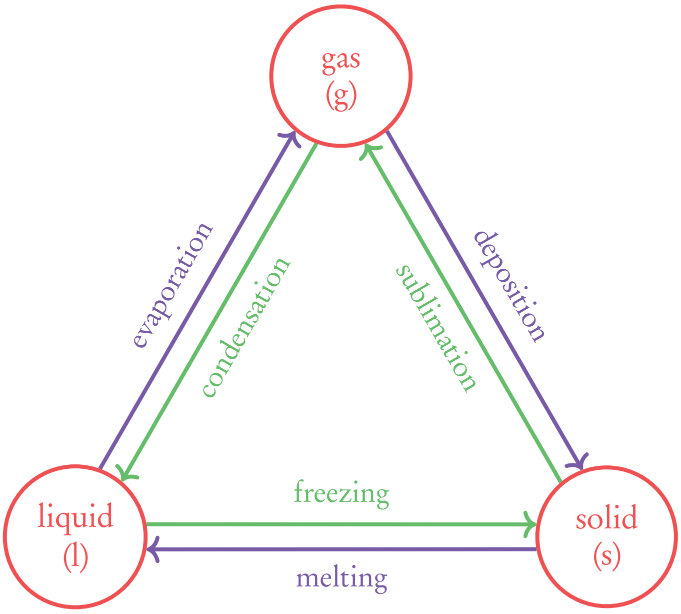
From the previous, derive the molecular formula if the molecular mass is $222.4\,\mathrm{g\,mol^{-1}}$.

1. $\frac{\text{molecular mass}}{\text{mass of the empirical formula}}$ $\frac{222.4\,\mathrm{g\,mol^{-1}}}{4\cdot 12.01 + 10\cdot 1.01 + 16.00\,\mathrm{g\,mol^{-1}}} = 3$

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*. Both C and H occur in one substance before and after the reaction arrow, so balance these first: $1\,C_{10}H_{22} + O_2 \longrightarrow 11\,H_2O + 10\,CO_2$

Next, balance O: $1\,C_{10}H_{22} + \frac{31}{2}\,O_2 \longrightarrow 11\,H_2O + 10\,CO_2$ (multiply by 2)

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

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:	A mole is a grouping of 6.0×10^{23}, so:
2 dozen is a grouping of 24.	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 arithmetic mean of all isotopes and their terrestrial 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.

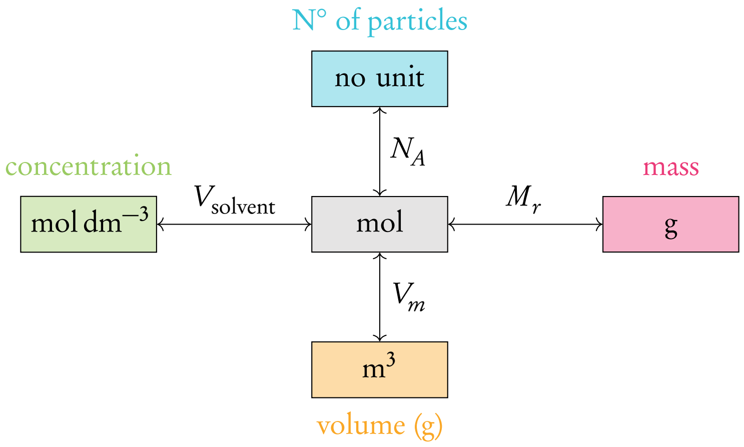
Molar mass M the mass of a substance *per one mole* expressed in g mol^{-1}

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

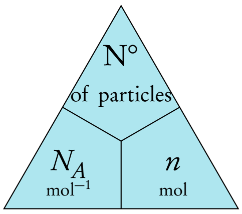
It is much easier to measure some physical quantity of a sample, such as its mass, than it is to count the number of particles in the sample. Therefore, you will have to convert various quantities to mole and back. The figure below gives an overview of the quantities that can be converted to moles and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

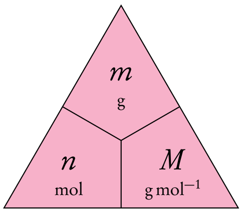
What is the total number of atoms in 0.20 mol of propanone, CH_3COCH_3?

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 g 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 [g mol^{-1}]

Example.

What is the amount in moles of 4.00 g in NaOH?

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

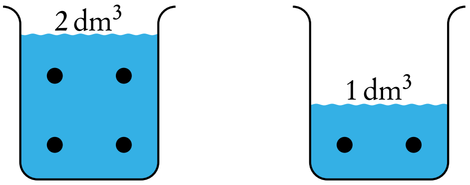
Mole ⟷ [concentration]

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 [...], and expressed in $mol\,dm^{-3}$

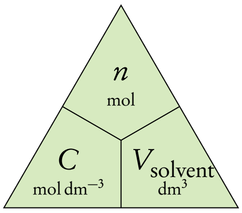
Standard solution a solution with a known concentration of solute

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

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

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	

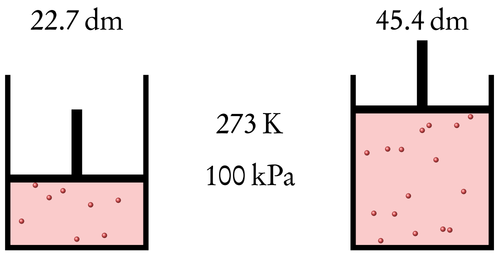
Mole ⟷ volume gas

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

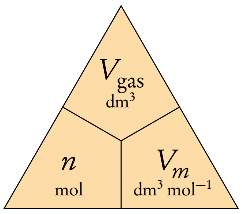
Molar volume (V_m) the volume of one mole gas, expressed in $dm^3\ mol^{-1}$ or $m^3\ mol^{-1}$, at a particular pressure and temperature.

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 $22.7\ dm^3\ mol^{-1}$.



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



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

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

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 $NaN_3 : N_2 = 2 : 3$, $\frac{2.50\ mol}{2} \times 3 = 3.75\ mol\ N_2$ forms.

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

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

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!

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]

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 $V_m = \frac{V}{n}$.

Rearrange the ideal gas law: $\frac{V}{n} = \frac{RT}{p} = V_m$

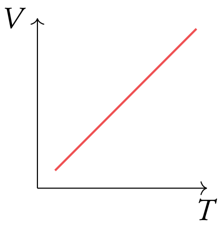
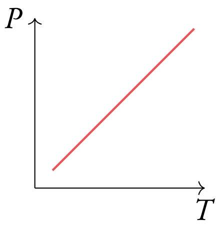
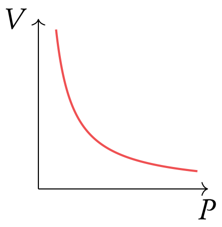
$$V_m = \frac{RT}{p} = \frac{8.31 \cdot 273\,\text{K}}{1.00 \times 10^5\,\text{Pa}} = 2.27 \times 10^{-2}\,\text{m}^3\,\text{mol}^{-1} = 22.7\,\text{dm}^3\,\text{mol}^{-1}$$

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. Mathematically, two situations $(_1)$ and $(_2)$ can be related by:

$$nR = \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

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

From $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ 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	$\frac{\cancel{p_1}V_1}{T_1}=\frac{\cancel{p_2}V_2}{T_2}$ $\frac{V_1}{T_1}=\frac{V_2}{T_2}$	$\frac{p_1\cancel{V_1}}{T_1}=\frac{p_2\cancel{V_2}}{T_2}$ $\frac{p_1}{T_1}=\frac{p_2}{T_2}$	$\frac{p_1V_1}{\cancel{T_1}}=\frac{p_2V_2}{\cancel{T_2}}$ $p_1V_1=p_2V_2$
relation	$V \propto T$	$p \propto T$	$p \propto \frac{1}{V}$
graph			

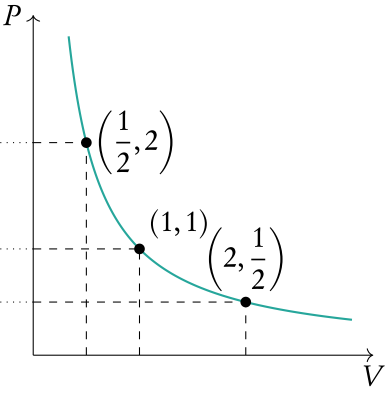
Example.

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

$p_1V_1 = p_2V_2$ holds, so put in some numbers to figure out the relation.

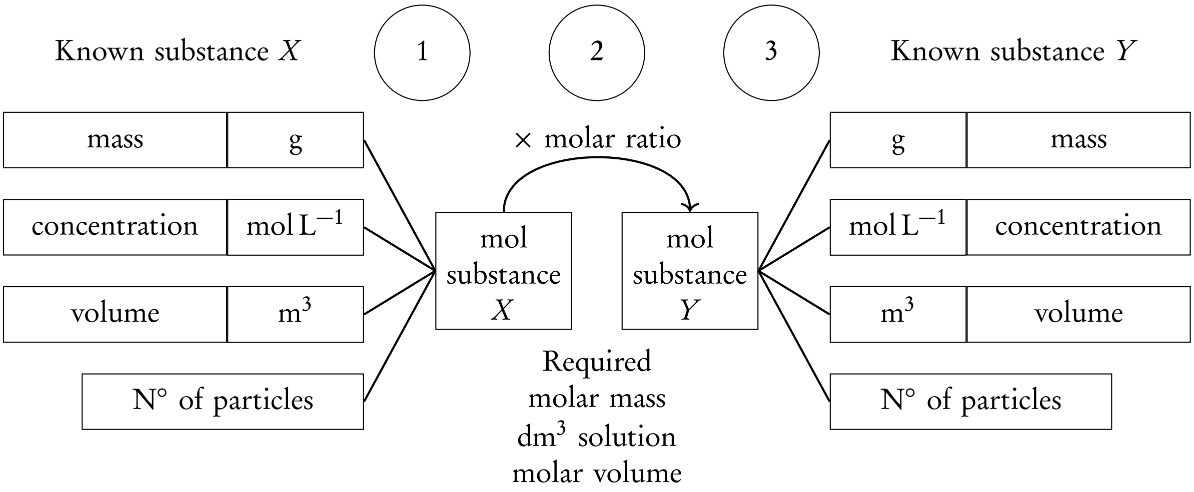
Assume $p_1V_1 = 1 \cdot 1 = 1$:

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



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	$CH_4 M_m = 12.0 + 4 \cdot 1.01 = 16.04\,\text{g mol}^{-1}$ $\frac{5.0}{16.04} = 0.312\,\text{mol}\ CH_4$
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 $0.312\,\text{mol}\ CH_4 \cdot \frac{3}{1} = 0.935\,\text{mol gas}$.
4.	Convert moles to required units	Under STP $V_m = 24.5\,\text{dm}^3\,\text{mol}^{-1}$, $0.935\,\text{mol} \cdot 24.5\,\text{dm}^3\,\text{mol}^{-1} = 22.9\,\text{dm}^3$
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 $\longrightarrow$ 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

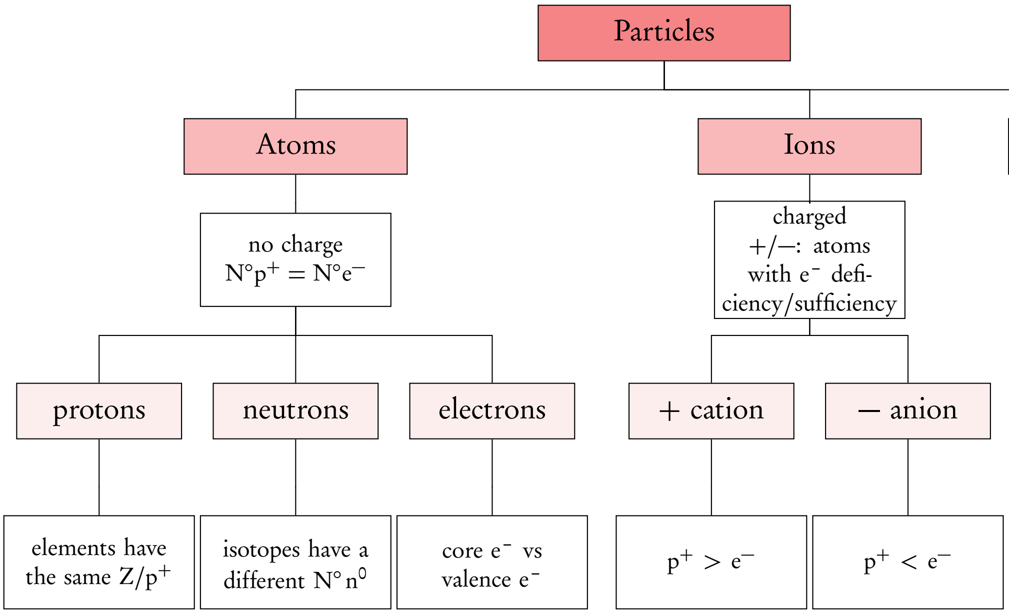
4.22 g Al reacts with 25.0 g Br_2 in the following reaction: $2Al + 3Br_2 \longrightarrow 2AlBr_3$. Identify the limiting reactant and use it to determine the theoretical yield of $AlBr_3$.

1.	Convert units to moles	$\frac{4.22\,\text{g}}{26.98\,\text{g mol}^{-1}} = 0.156\,\text{mol Al}$ $\frac{25.0\,\text{g}}{2 \cdot 79.90\,\text{g mol}^{-1}} = 0.156\,\text{mol Br}_2$
2.	Divide the number of moles of each reactant by its reaction coefficient. The reactant with the lowest result will be the limiting reactant.	$\text{Al:}\frac{0.156\,\text{mol}}{2} = 0.078$ $\text{Br}_2\text{:}\frac{0.156\,\text{mol}}{3} = 0.052$ 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 $0.156\,\text{mol} \cdot \frac{2}{3} = 0.104\,\text{mol AlBr}_3$

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^+

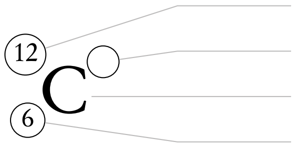
Positive ion/cation ⊕ contains *less* e^- than p^+

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 $= N°p^+ + N°n^0$

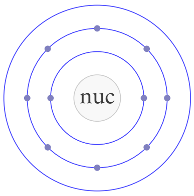
charge: e^- deficiency/sufficiency

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?



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

⊖ 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

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

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

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 $^{71}\text{Ga} = 1 - x$

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

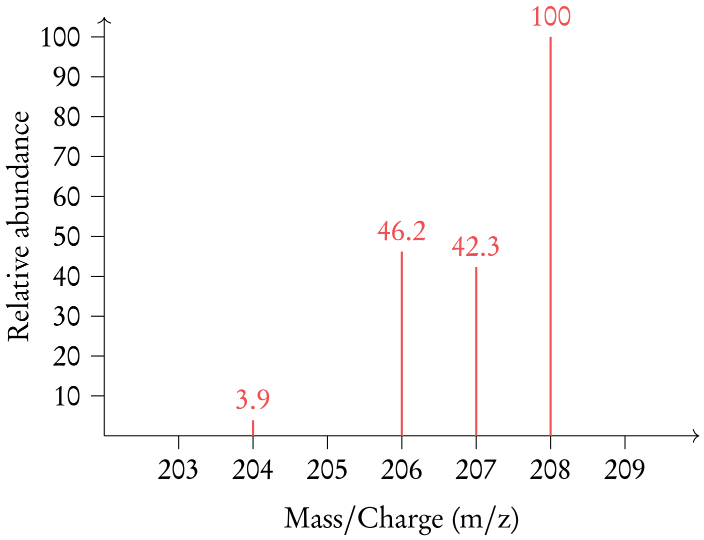
$$69.72\,\text{g}\,\text{mol}^{-1} = x \cdot 69 + (1-x) \cdot 71 = 69x + 71 - 71x$$

$$x = 0.64$$

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.

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

2.4 Atomic shells/subshells/orbitals

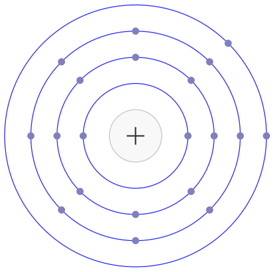
Electron shell is also often referred to as the *main energy level*

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 particular 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	max. N° of e^-	N° of orbitals					electron
n	$2n^2$	s	p	d	f	total	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	$4s^x\ 4p^x\ 4d^x\ 4f^x$

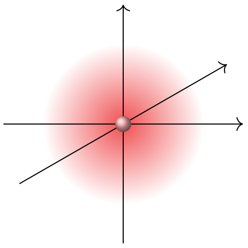


The principal electron shells can be imagined as an onion: the first shell ($n = 1$) is closest to the nucleus and each of the following shells is further away. The shells are numbered: $n = 1$, $n = 2$, …

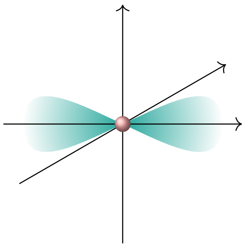
Every shell contains the s subshell, from the second shell ($n = 2$) forward all shells contain the p subshell, from the third shell ($n = 3$) all shells contain the d subshell etc.

The shape of the subshells

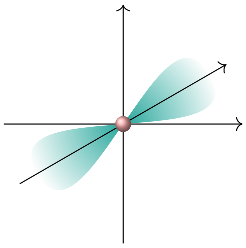
Every s subshell consist of one spherical orbital, which is further away from the nucleus the higher the shell number. The p subshell always contains 3 orbitals which are aligned along the xyz-axis. Since the second shell ($n = 2$) contains the 2s 2p subshells which can host 2 and 6 electrons respectively,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



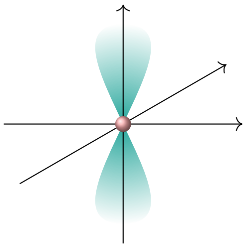
s orbital



p_x orbital



p_y orbital



p_z orbital

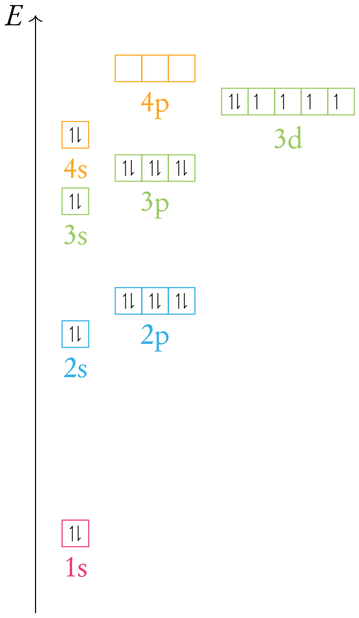
2.4.1 Electron configuration

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

Aufbau principle = 1s 2s 2p 3s 3p 4s 3d 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.



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

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: $[Ar]\ 4s^2\ 3d^6$

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

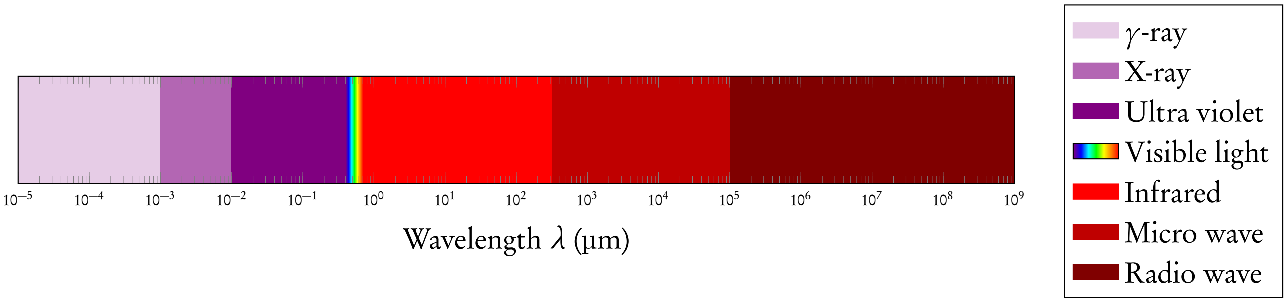
$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda}$$

E_{photon} = energy of a photon [J]

h = Planck's constant 6.63×10^{-34} J s

ν or f = frequency $[s^{-1}]$

λ = wavelength [m]

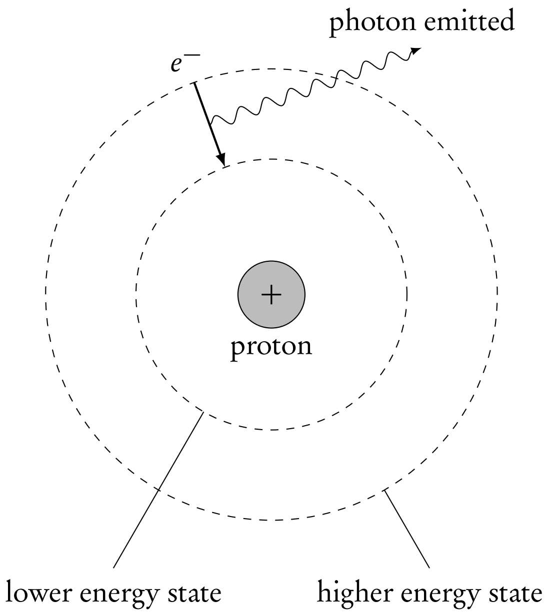


Visible light (Vis) is an example of electromagnetic (EM) radiation. The colour of light is tied to the amount of energy of a photon. But visible light is only a small part of the EM spectrum; at the higher energy end of the spectrum we find ultraviolet (UV), X-ray and γ-ray, at the lower energy end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

Electron energy levels

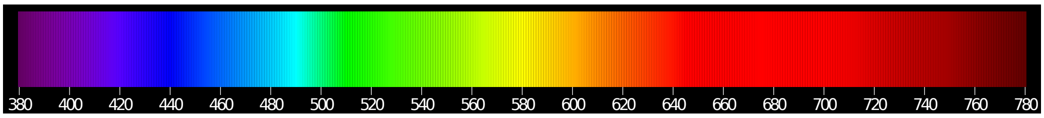
The energy level of an electron depends on which atomic orbital it occupies. The lowest energy level is called the groundstate; an electron can move to a higher energy level (excited state) by absorption of a photon. And similarly, an electron can move from an excited state to a lower energy level by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

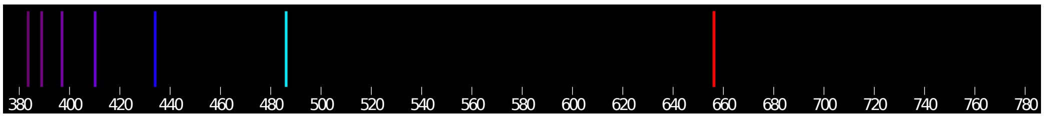


When excited electrons 'fall' from a higher to a lower energy state, photons with a discrete amount of energy are emitted. The emission spectrum of atoms is a line spectrum: only light of a particular colour (discrete energy) is emitted.

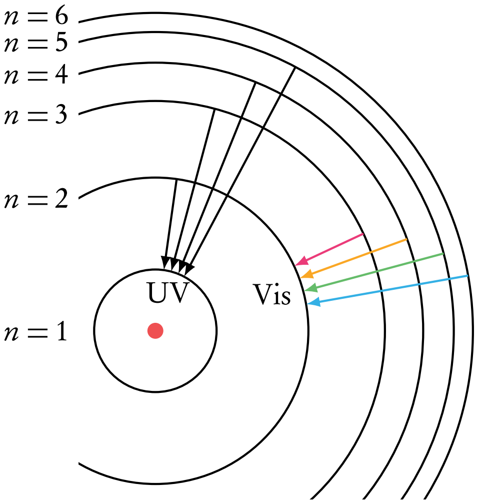
Continuous spectrum

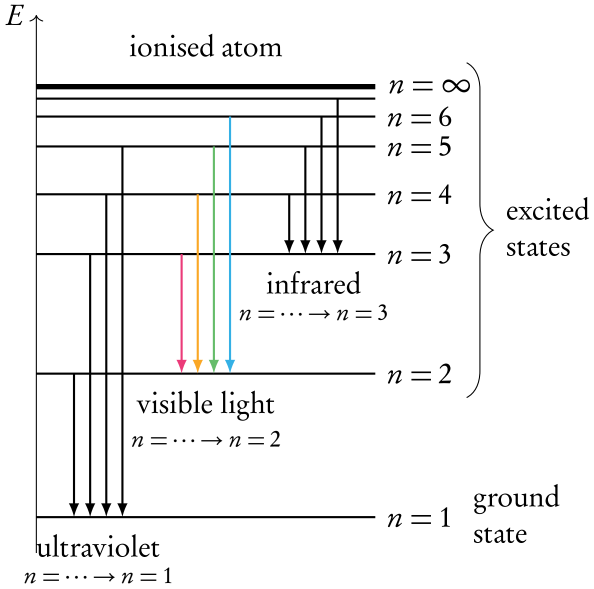


Hydrogen



Hydrogen energy levels





Electrons that 'fall' to the groundstate ($n = 1$) emit photons with the greatest amount of energy (UV radiation). 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 energy levels converge at higher energy: the difference between the energy levels becomes smaller up to the point where the difference is 0. The energy difference between the *more energetic photons* is increasingly smaller. Therefore line spectra *converge at higher energy.*

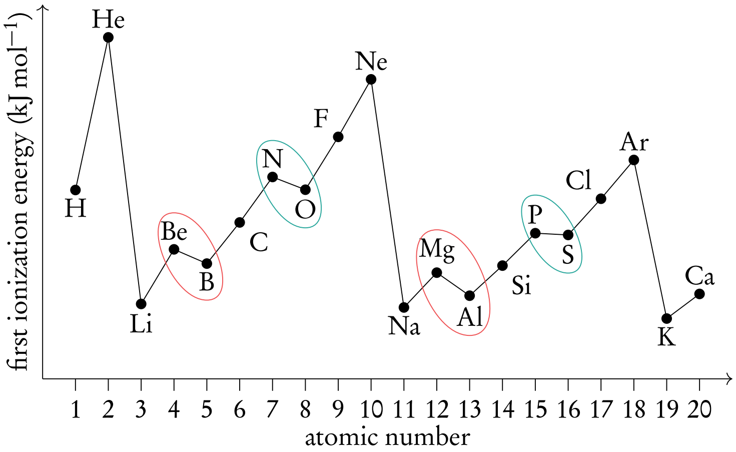
2.6 Ionization energies

First ionization energy the energy required to remove *one mole electrons* from *one mole of gaseous atoms*, to produce *one mole of gaseous 1+ ions*.

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.

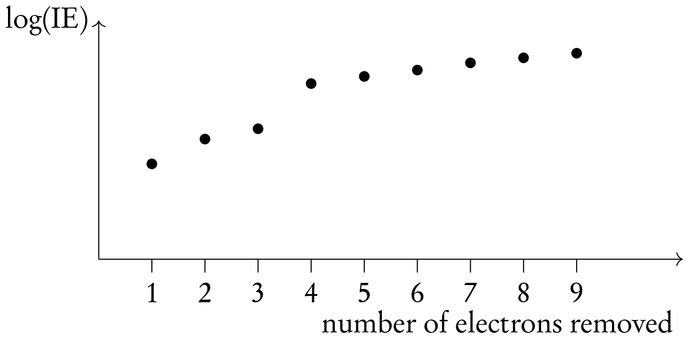
Evidence for subshells

From Be [He]s^2 to B [He]s^2p^1: an electron is added to the p-subshell, which has a slightly 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.

Successive ionisation energies

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



In the figure above we see the abrupt 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.

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.

PERIODICITY

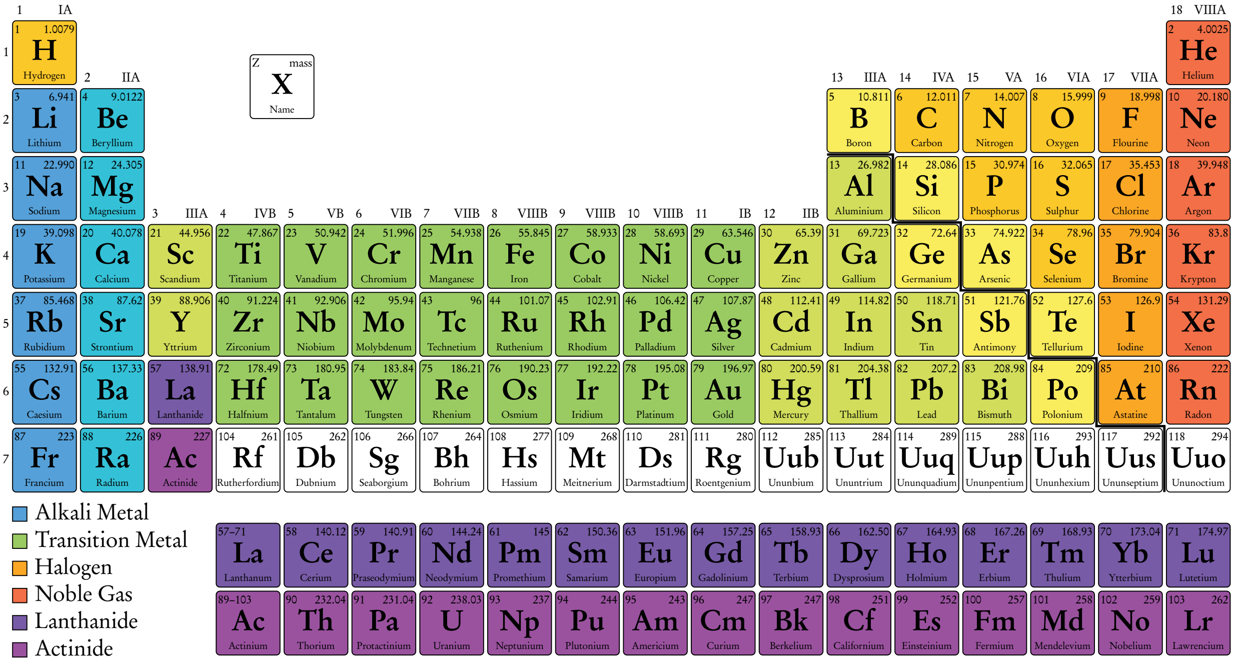
3

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



	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	57 138.91 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	89 227 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

57–71 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
89–103 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

Z mass
X
Name

🟦 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.

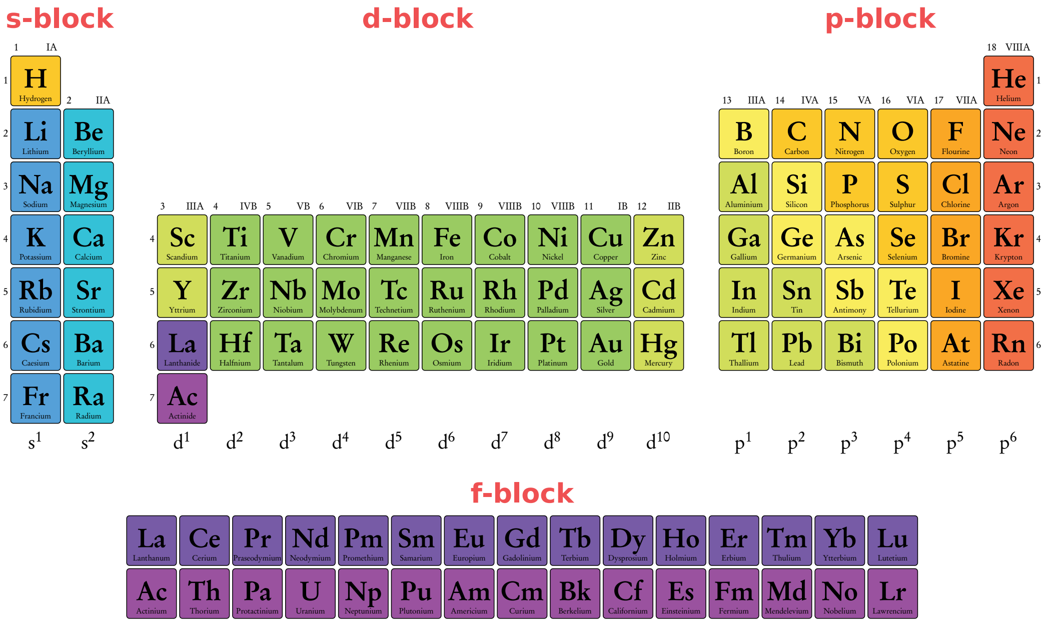
Subshells & blocks

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



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

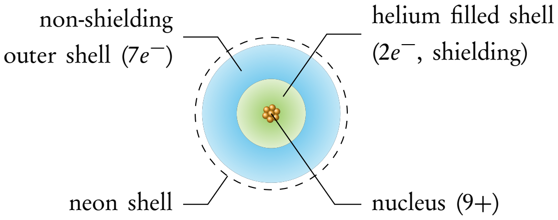
3.2 Periodic trends

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 ⊕-charge that the valence electrons experience

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

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



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

Example.

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

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

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

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

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

${}_{17}$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.

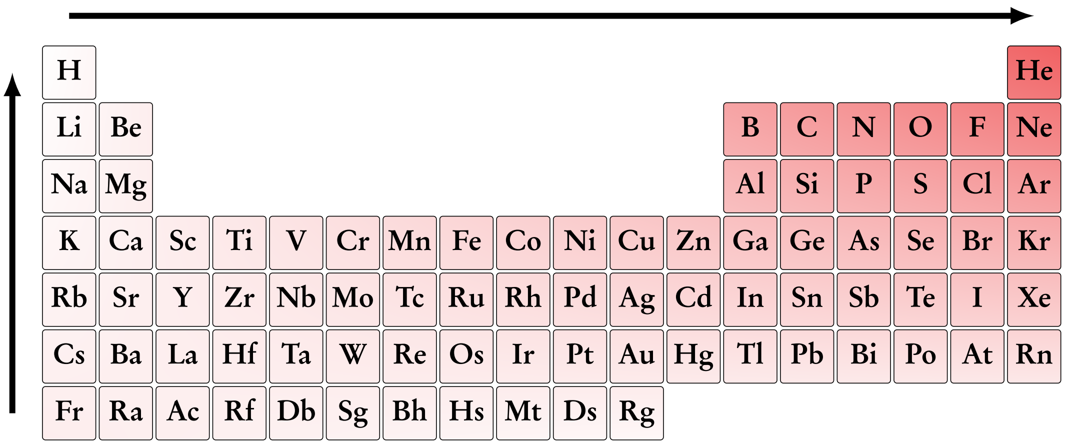
The valence electrons mutually repel each other. This repelling force increases when there are more electrons in the valence shell.

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 ↓.

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.

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.*

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 ↑.

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.

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 ↑.

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	$2\,Li + 2\,H_2O \longrightarrow 2\,LiOH + H_2$ $2\,Na + 2\,H_2O \longrightarrow 2\,NaOH + H_2$ $\dots$	forms alkaline solutions and H_2 which can combust (violently)
Alkali metals + halogens	$2\,Na + Cl_2 \longrightarrow 2\,NaCl$ $2\,K + F_2 \longrightarrow 2\,KF$ $\dots$	forms ionic halides, more reactive alkali metals + more reactive halogens produce a more vigorous reaction
Displacement reactions	$2\,KBr + Cl_2 \longrightarrow 2\,KCl + Br_2$	the more reactive halogen displaces the ions of the less reactive halogen
Ionic reactions	$\left\{\begin{array}{l} 2\,Br^- + Cl_2 \longrightarrow 2\,Cl^- + Br_2 \\ 2\,I^- + Cl_2 \longrightarrow 2\,Cl^- + I_2 \\ 2\,I^- + Br_2 \longrightarrow 2\,Br^- + I_2 \end{array}\right.$	

Table 3.1: Reactions involving Halogens and Alkali Metals

3.3 Transition elements

Transition elements an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell. Ions of transition elements have characteristic properties due to thier partially filled d-subshell.

Zn, though part of the d-block, is not a transition metal. The common oxidation state is Zn^{2+} which does not have a partially filled d-subshell. Instead, both Zn and Zn^{2+} have a completely filled d-subshell.

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

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

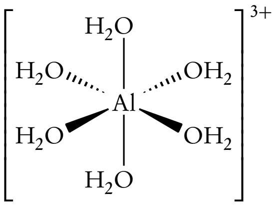
Variable oxidation states

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.

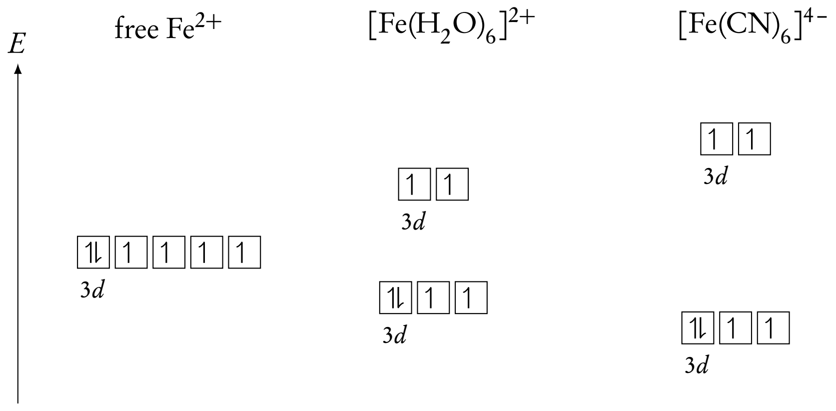
Complexes do not only form between ions and water molecules, but can form with many other substances so long as the ligand can donate an electron pair (lewis base). E.g. ammonia readily displaces water ligands, because it can form stronger dative covalent bonds than water.

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.

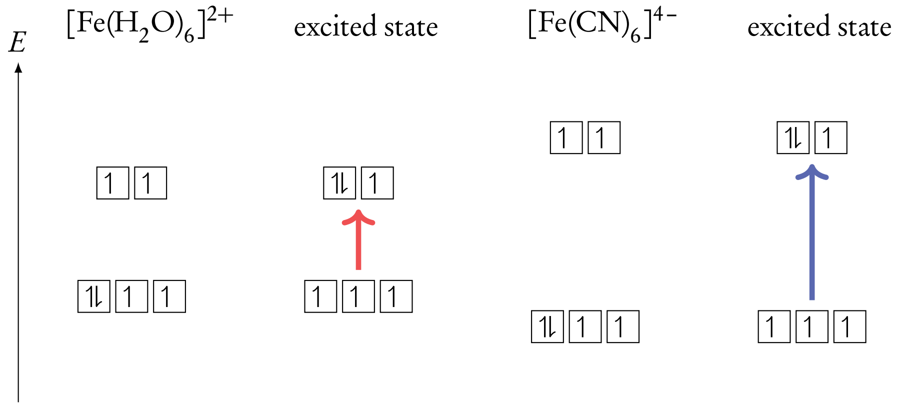


Note that the CN^- ligands cause a larger splitting of the d-orbital energy level because they form stronger bonds

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

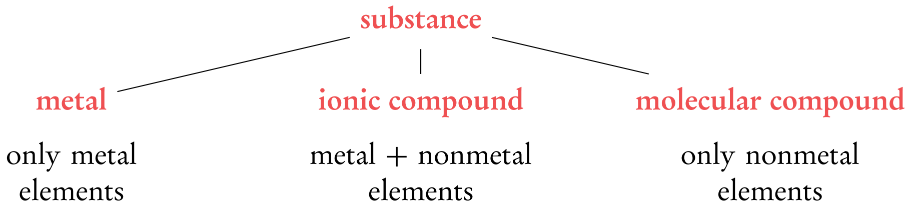
When orbitals are partially filled, often (some of) the electrons in the orbitals are unpaired. Each electron has a spin, which when two electrons are paired cancel each other out. When electrons are unpaired each produces a tiny magnetic field. When those spins line up in a material they can produce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

BONDING

4

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:



Electrostatic 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 difference is greater, or when
- 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 physical (macroscopic) properties of a substance are a consequence of the bonding and arrangement of particles (microscopic properties).

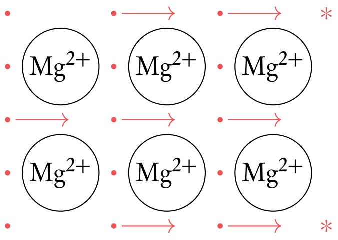
Physical properties

melting point (MP) & boiling point (BP): increases as bond strength 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



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:

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

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.

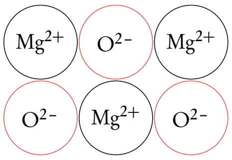
In alloys, the presence of foreign metal atoms disturb the host metal lattice structure, causing it to become harder to slide over each other. Alloys are less malleable.

4.2 Ionic bonding

Ions form when electrons are transferred from one element to another (redox):

- reducing the number of valence electrons, to form a metal cation
- increasing the number of valence electrons, to form a non-metal anion

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



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:

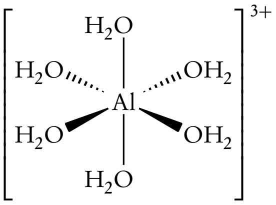
- when the ionic *charge is larger*, and
- with *smaller size* of the ions.

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.

4.2.1 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^-		

Memorize 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

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.

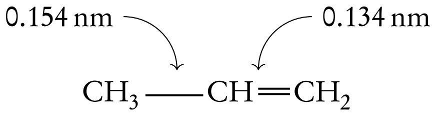
While hydrogen achieves the noble gas configuration with 2 electrons in its outer shell, other non-metal atoms require 8 e^- in their valence shell to achieve the noble gas configuration. To determine bonding of those elements we use the octet rule.

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 the table below, the bond strengths and lengths of single, double and triple bonds are compared. Stronger bonds are shorter. Note that a double bond is *less then* twice as strong as a single bond.

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



CH_3—$CH{=}CH_2$

Nomenclature of simple 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 more electronegative atom is written lastly and is suffixed by *-ide*.

Example.

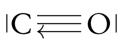
Molecular formula	Systematic name	Trivial name
H_2O	dihydrogen oxide	water
CO_2	carbon dioxide	
CO	carbon monoxide	
S_2Cl_2	disulfur dichloride	

Coordinate covalent bond = dative bond

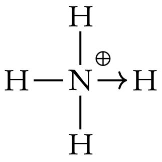
Dative Bond one atom *donates a non-bonding pair* forming a covalent bond (instead of both of the atoms donating 1 electron). Such a bond can be indicated by an arrow →.

Example.

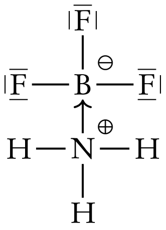
CO



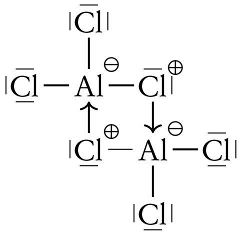
NH_4



NH_3BF_6



Al_2Cl_6



4.3.1 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 atoms tend to form a stable arrangement with 8 electrons in their valence shell = 4 e^--pairs, corresponding to the noble gas configuration.

Importantly, some elements never deviate from the octet rule while others regularly do. This has to do with the max. number of electrons that are allowed in the valence shell: first period elements (H) in the periodic table have no more than 2 valence electrons, and second period elements (B, C, N, O, F) can never have more than 8 valence electons.

But elements from the third period and further can have expanded octets, meaning that they have more than eight electrons around one atom. This is possible because the 3rd-shell can have a total of 18 electrons. To summarize:

- H will have max. 2 electrons in its valence shell = surrounded by 1 e^--pair
- B will oftentimes have only 6 electrons in its outer shell = 3 e^--pairs.
- C, N, O & F will *always* obey the octet rule.
- P, S, Cl, Br & I and other non-metal elements beyond the 3rd period prefer to have an octet, but can expand their octet to have up to 18 electons in their valence shell.

How to draw Lewis structures

1 → **Calculate the total number of valence electrons** → electron pairs.

- derive the number of valence electrons from the group number of the element;
- add the charge of anions or subtract the charge of cations.

2 → **Draw the most likely structure of the molecule.**

- the central atom is usually the least electronegative atom;
- refrain from drawing cyclic compounds, unless explicitly stated.

3 → **Add lone pairs to the outer atoms, until each has an octet (or duets for H).**

- place remaining lone pairs on the central atom (expanded octet);
- if the central atom has fewer electrons than an octet, exchange lone pairs from the outer atoms to form double or triple bonds to the central atom to achieve an octet;
- resonance occurs when the double bond can be placed in multiple equivalent positions.

4 → **Determine the formal charge (FC) *on each atom separately*.**

- formal charge = 0 when atoms have their *regular number of bonds*, e.g. H: 1 bond, C: 4 bonds, N: 3 bonds, O: 2 bonds, F: 1 bond etc.
- formal charge = number of valence electrons − 1 × number of bonds
  − 2 × number of lone pairs
- the formal charges should add up to the overall charge of the molecule or ion.

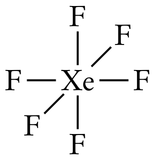
Example.

Draw the Lewis structure of XeF_6.

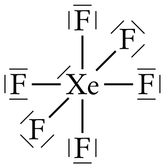
1 → Number of valence electrons of Xe = 8 and F = 7

$8 + 6 \cdot 7 = 50\,\text{ve}^-$
or 25 e^--pairs

2 → Draw the most likely structure of the molecule.
Xe has lower electronegativity than F



3 → Make octets on the outer atoms and add the remaining lone pair(s) to the central atom.



4 → The formal charge of each atom is 0.

5 → The octet is already expanded.

Resonance structures

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.

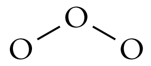
Example.

Draw the Lewis structure of O_3 and show the resonance structures and the resonance hybrid.

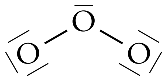
1. The number of valence electrons of $O = 6$

$3 \cdot 6 = 18\,\text{ve}^-$
or 9 e^--pairs

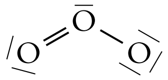
2. Draw the most likely structure of the molecule.



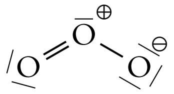
3. Make octets on the outer atoms and add the remaining lone pair to the central atom.



Form an octet on the central atom by exchanging a lone pair for a double bond.

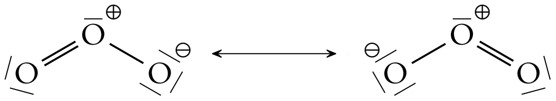


4. Determine the formal charge on each atom.

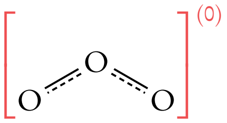


5. The octet cannot be expanded.

In step 3 the placement of the double bond on the left or right of the central atom is arbitrary. The *real* structure of ozone has an electron distribution that is the mean of the two possible structures, which can be represented by the resonance hybrid.



or



resonance hybrid

The resonance hybrid shows the distribution of the double bond over the two O$\overset{\text{---}}{=}$O bonds. Resonance hybrids must *always* be drawn with: 1. square brackets around them, 2. without any lone pairs and 3. without the formal charges. And 4. if the overall charge is not 0 it must be indicated on the top right.

4.3.2 VSEPR: shapes of molecules and ions

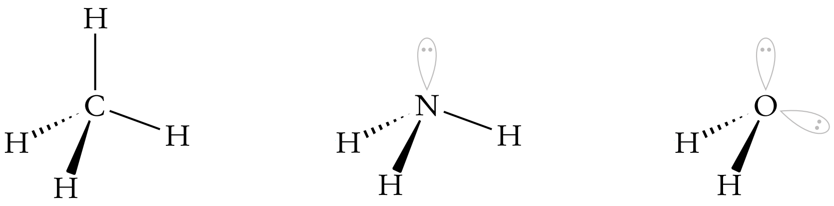
Electron domain every bonding or non-bonding pair surrounding an atom. Single, double and triple bonds *count as 1 electron domain*, because they are situated between two atoms in the same 'spatial domain'

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 4.1



109.5°
methane

107°
ammonia

104.5°
water

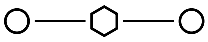
Methane, ammonia and water each have tetrahedral electron domain geometry. But with increasing number of lone-pairs, they have different molecular geometries.

Electron domain geometry the 3d arrangement of atoms *and* lone pairs.

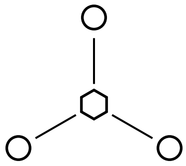
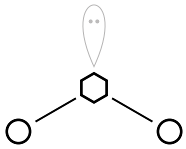
Molecular geometry the 3d arrangement of *only* atoms.

In the table below the central atom is draws as ⬡ and the surrounding atoms as ○. The lobe with two dots  represents a lone pair.

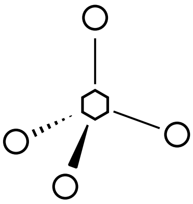
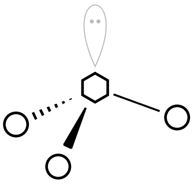
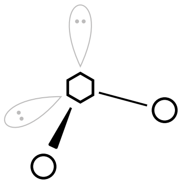
② Electron Domains: linear ED geometry

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

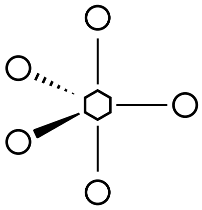
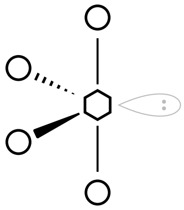
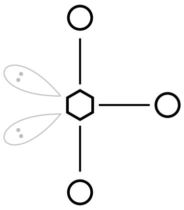
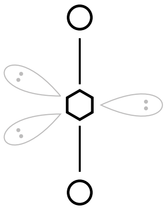
③ Electron Domains: trigonal planar ED geometry

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°	

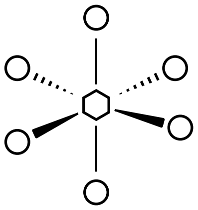
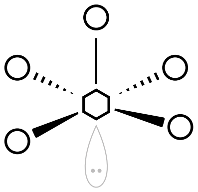
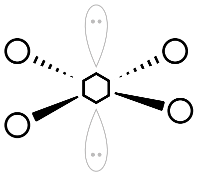
④ Electron Domains: tetrahedral ED geometry

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 Domains: trigonal bipyramidal ED geometry

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 Domains: octahedral ED geometry

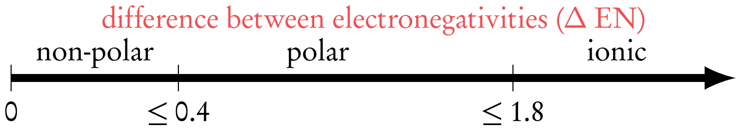
Bonding pairs	Non-bonding pairs	Name of the molecular shape (atoms only)	Bond angle	Molecular shape
6	0	octahedral	90°	
5	1	square pyramid	90°	
4	2	square planar	90°	

Polar bonds: from covalent to ionic 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 ($\delta+$).



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 to form ions)

Whether a bond is covalent or polar covalent *inside* a molecule, determines the type of bonding *between* molecules → intermolecular forces dictate the 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)*

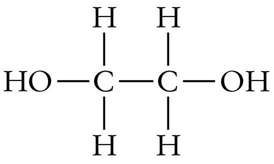
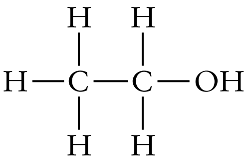
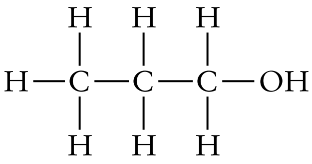
4.4.1 Hydrogen bonding

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 4.1.

Table 4.1

	1,2-ethanediol	ethanol	1-propanol
Structure	 $HO-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$	 $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-OH$
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 δ+ and δ+

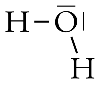
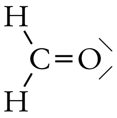
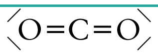
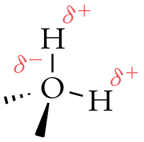
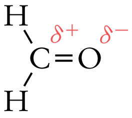
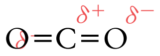
Dipole-dipole bond electrostatic attraction between the partial charges of two dipole molecules

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

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.

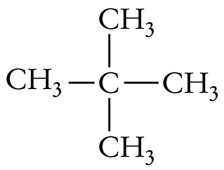
London Dispersion (LD) forces electrons oscillate in all molecules, causing a temporary instantaneous dipole. This in turn can induce a temporary instantaneous dipole in a neighbouring molecule, resulting in a weak electrostatic attraction between the molecules

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.

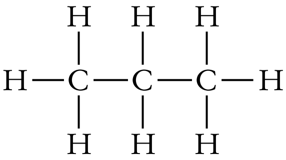
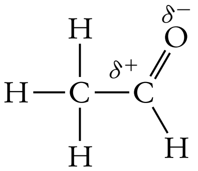
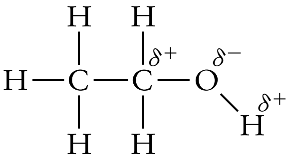
The LD forces increase as the polarisability of molecules increases:
- as the number of electrons increases = the mass of a molecule increases.
- as the surface area of a molecule increases. Branched molecules have a smaller surface area, are less polarizable, so they experience smaller LD forces.

	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
 $CH_3{-}C(CH_3)_2{-}CH_3$	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	$44\,g\,mol^{-1}$	$44\,g\,mol^{-1}$	$46\,g\,mol^{-1}$
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

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.

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).

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

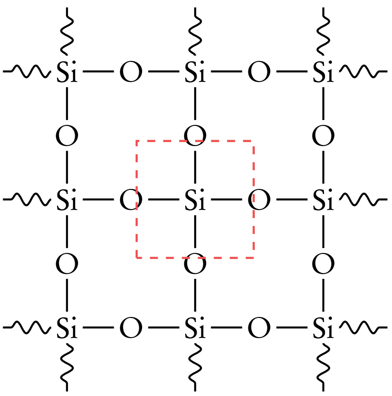
Giant covalent structures all the atoms are bonded by covalent bonds in a continuous network extending throughout the material

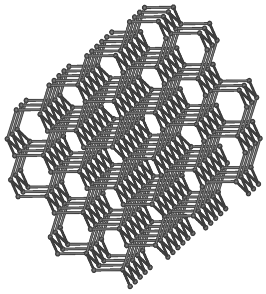
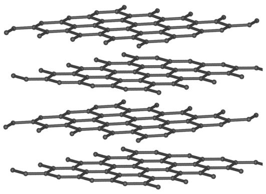
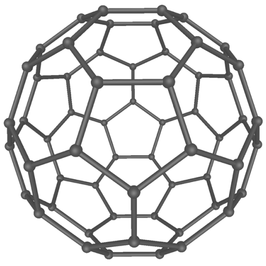
Allotropes occur when an element can exist in different crystalline forms.

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

Examples of giant covalent structures are diamond and graphite (discussed below), Si (which is like diamond) and SiO_2 known as 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



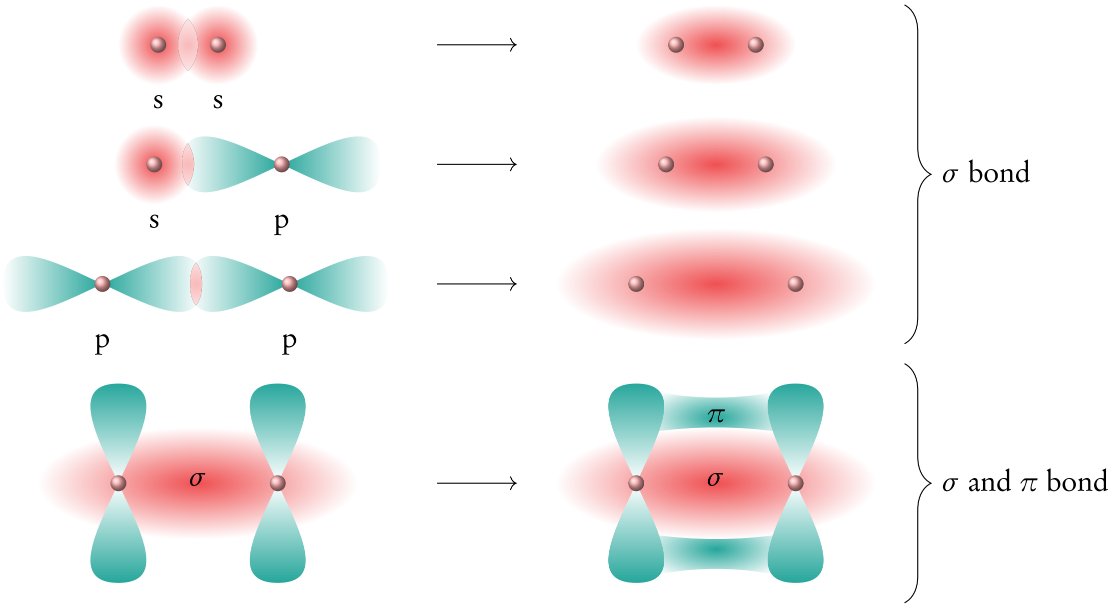
allotropes of C	Diamond	Graphite	Fullerene
			
macrostructure	network	stacked flat layers of hexagonal C lattices	hexagonal C lattice folded in on itself
shape	tetrahedral	trigonal planar	trigonal planar
bond angles	109.5°	120°	$< 120°$
bonds	single bonds	1× double bond	1× double bond
conduction	no, 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

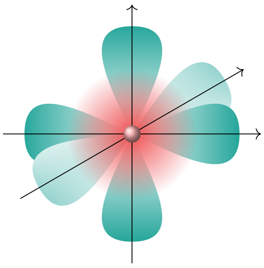
Hybridization the mixing of atomic orbitals of different energy to obtain homogeneous orbitals of the same (degenerate) energy

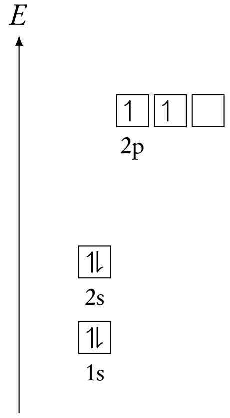
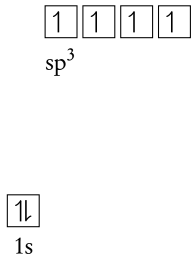
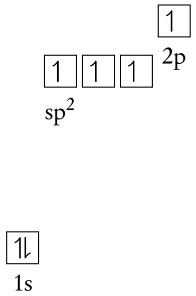
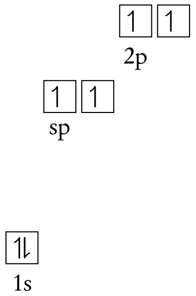
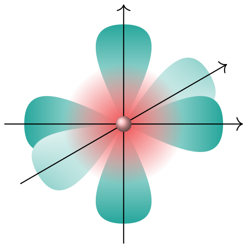
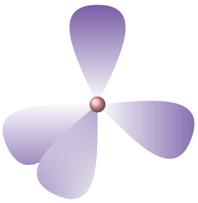
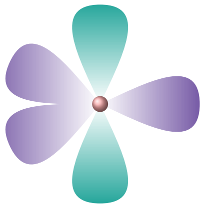
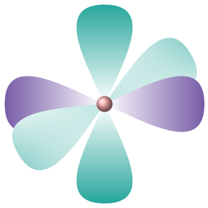
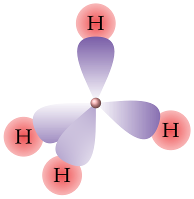
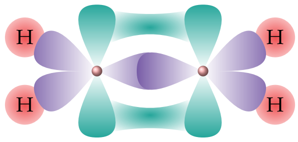
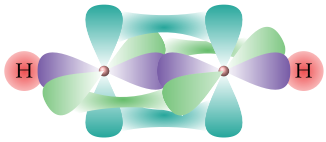
The atomic s and p orbitals mix to form new hybrid orbitals, to form covalent bonds with other atoms. The shape and energy level of the new orbitals are a mix of the constituent s and p atomic orbitals.

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

Photodissociation	chemical bonds absorb enough light energy to break.
Radical	a highly reactive molecule that contains an unpaired electron.

Ozone absorbs UV light, protecting us from its ionizing effects (UV light possesses sufficient energy to separate an e^- from molecules, which can cause e.g. skin cancer). 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 catalyse the depletion of zone, and have disrupted the steady state.

Formation of ozone

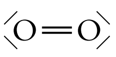
Ozone is continuously produced naturally in the stratosphere by the photodissociation of oxygen. The strong O=O bond requires high energy UV light to break the bond, forming two O atoms. The O atoms will react with O_2 molecules forming ozone O_3.

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

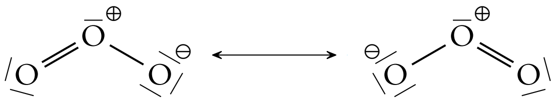
Ozone protection mechanism

As discussed in section 4.3 covalent bonding; double bonds are stronger than single bonds. And the strength of the resonant bonds in ozone lie between that of a single and double bond (bond order 1.5).

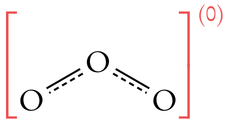
Remember:
bond strength & length are equal due to resonance.



oxygen



ozone resonance structures



ozone resonance hybrid

To break a $\text{O}\overset{\cdots}{-}\text{O}$ bond in O_3, less energy is required than to break the O=O bond in O_2. So while oxygen can absorb high energy UV light with wavelengths < 240 nm, ozone absorbs wavelengths < 390 nm, thus offering protection against medium energy UV light with wavelengths between 240 nm to 390 nm.

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

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

Ozone is regenerated 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.

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

Depletion of ozone

Radicals form due to the homolytic fission of a covalent bond, leaving the two fragments 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.

Similarly 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.

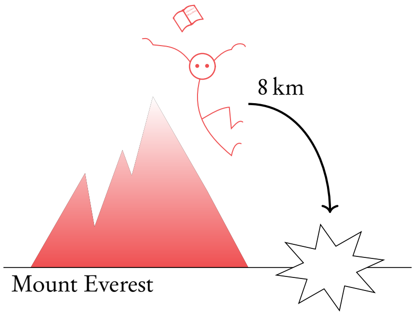
Read "enthalpy" as "chemical energy"

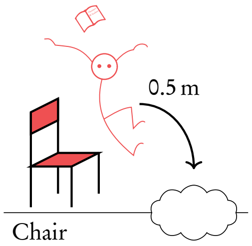
Higher enthalpy: substance has weaker bonds, can release more heat.	**Lower enthalpy:** substance has stronger bonds, can release less heat.

The absolute value of enthalpy cannot be measured, so we measure the *enthalpy change* (ΔH) between products and reactants in 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.





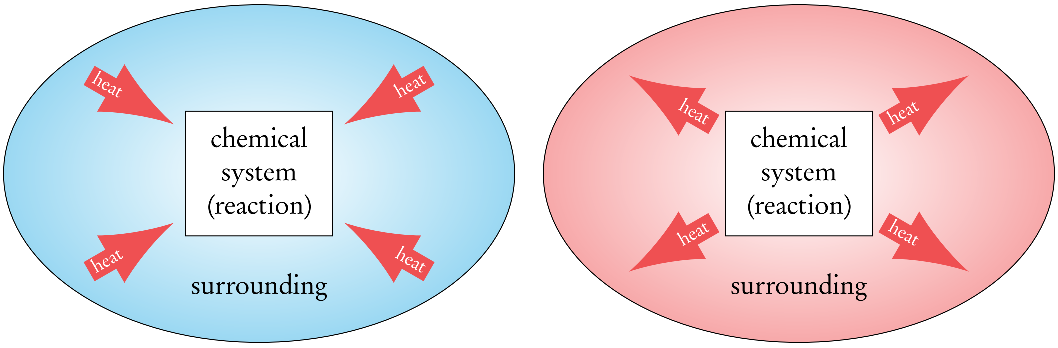
Although the stickman on top of the mountain has a huge amount of potential energy, this has no effect on the amount of his kinetic energy at the top. The kinetic energy (of his fall) depends on the *height difference*.

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 system 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:

$$\Delta Q = c m \Delta T$$

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:

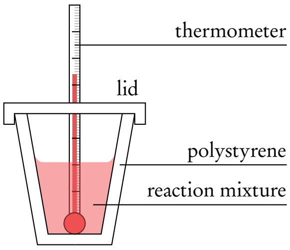
$$\Delta H = -\frac{\Delta Q_{\text{surrounding}}}{n_{\text{system}}}$$

ΔH = enthalpy change $[\text{kJ mol}^{-1}]$
$\Delta Q_{\text{surrounding}}$ = 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.

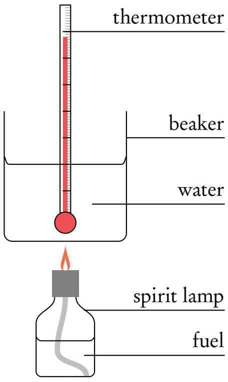
Calorimetry is a technique to measure the increase or decrease in heat by measuring the temperature change of the surrounding, typically that of water ($c = 4.18\,\text{J g}^{-1}\,\text{K}$). Under the assumption that no heat is lost, the enthalpy change of a chemical reaction can be calculated from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

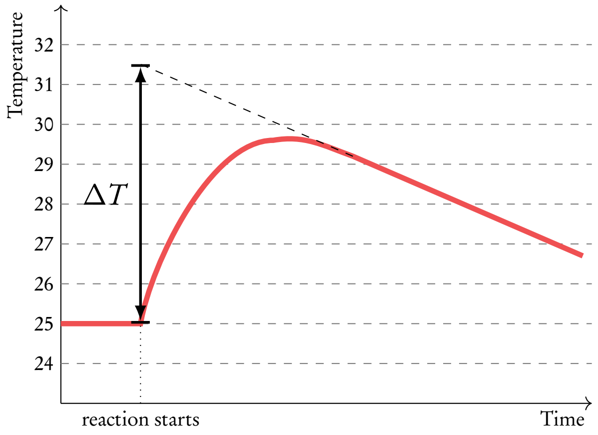
Calorimetry: combustion



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 ΔH. 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 $\Delta H =$ negative, which is logical because all combustion reactions are exothermic

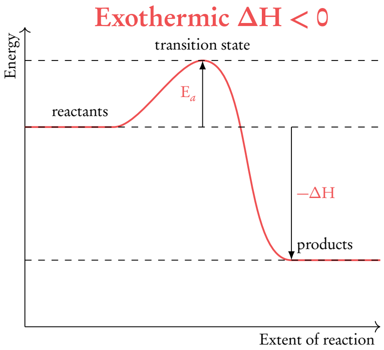
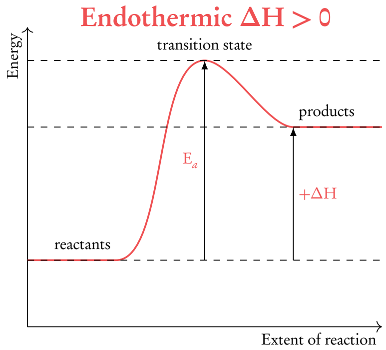
5.2 Energy diagrams

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 independent of the reaction pathway.

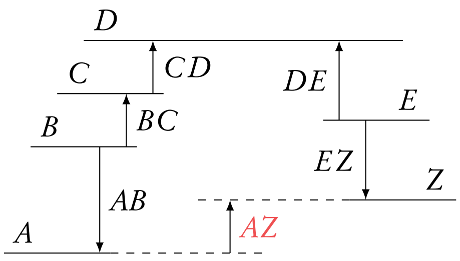


Figure 5.1

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.

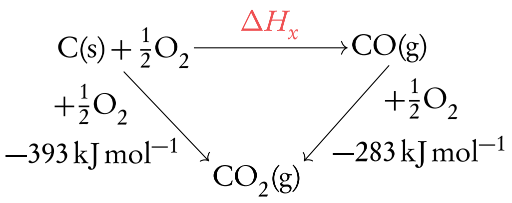


Figure 5.2

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.

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

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:

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

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

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

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

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

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 $2NO_2 \longrightarrow N_2O_4$.

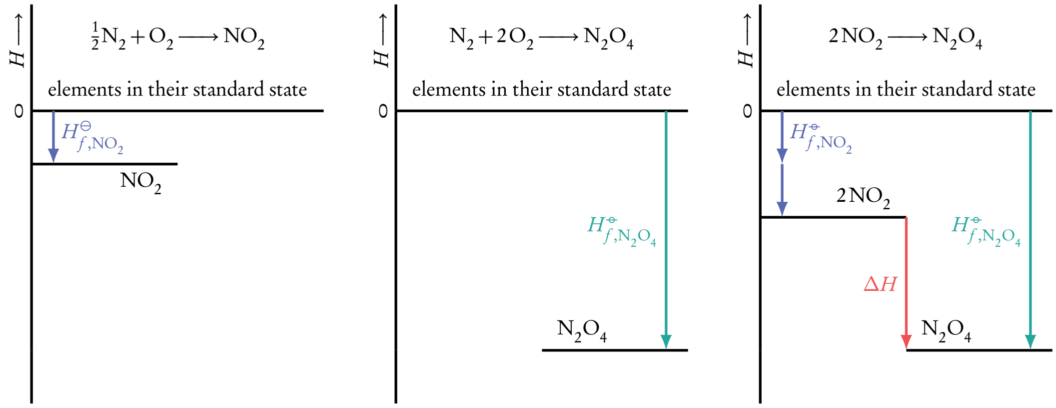


Figure 5.3

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 gaseous 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), …)

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: $\frac{1}{2}H_2O(g) \longrightarrow H(g) + \frac{1}{2}O(g)$

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

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 $H_2 + F_2 \longrightarrow HF$.

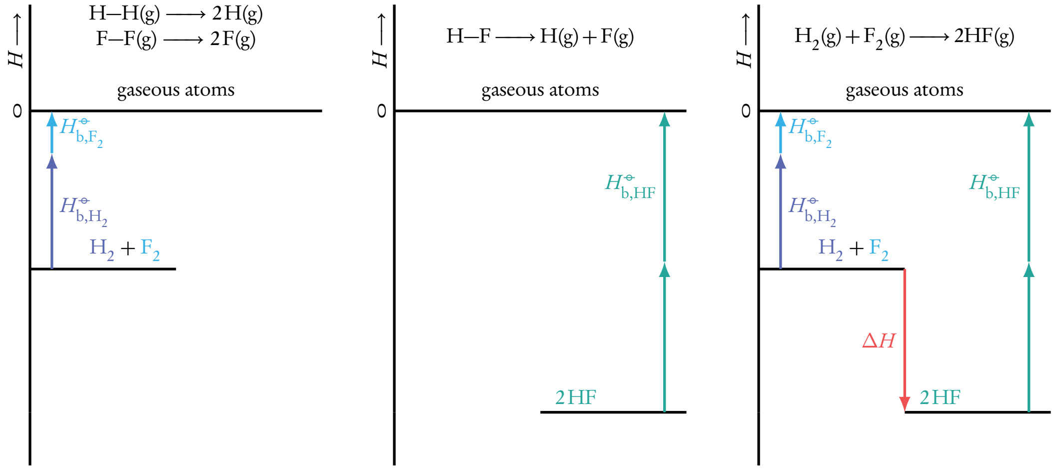


Figure 5.4

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 $C_2H_4 + H_2 \longrightarrow C_2H_6$.

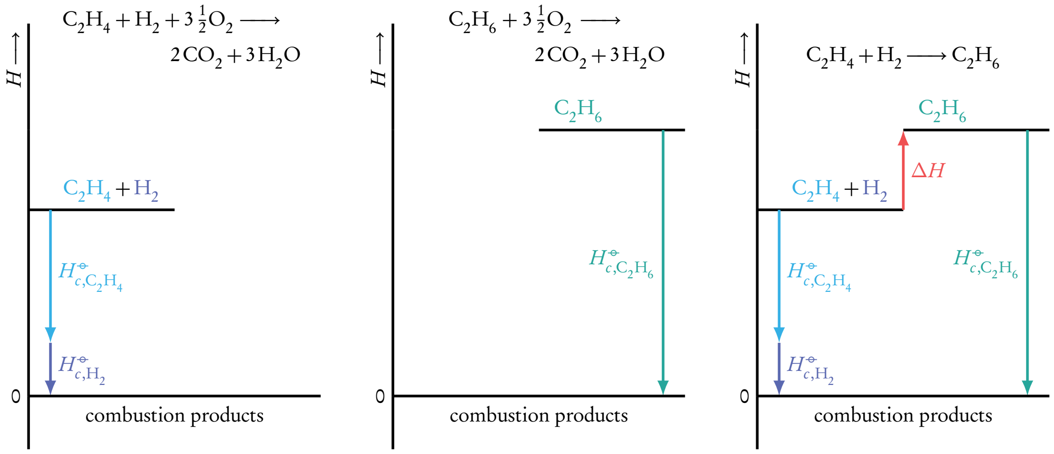


Figure 5.5

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

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
$\Delta H =$	$\sum H^\ominus_{\text{f,prod}} - \sum H^\ominus_{\text{f,react}}$	$\sum H^\ominus_{\text{b,react}} - \sum H^\ominus_{\text{b,prod}}$	$\sum H^\ominus_{\text{c,react}} - \sum H^\ominus_{\text{c,prod}}$

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:

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

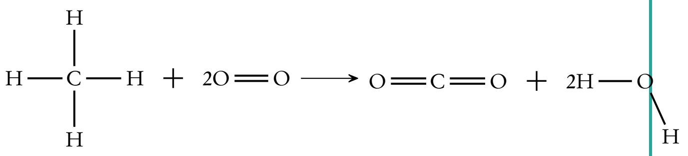
1.	Write the reaction equation	$C_2H_6(g) + Cl_2(g) \longrightarrow C_2H_5Cl(g) + HCl(g)$
2.	Find the enthalpy values (DB. 11-13) *remember:* when is $H = 0$?	$-84 \quad 0 \quad -137 \quad -92.3$
3.	Calculate $\sum H_{\text{reactant}}$ and $\sum H_{\text{product}}$ *separately*	$\sum H_{\text{reactant}}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

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*



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

$C{-}H$: 414

$O{=}O$: 498

$C{=}O$: 804

$O{-}H$: 463

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

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

× 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 $H = 0$?

$-874 \qquad -891 \qquad 0$

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

× number of molecules

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

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

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 65.

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

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

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

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

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*.

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*.

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

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

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

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

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

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

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.

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

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.

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

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

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

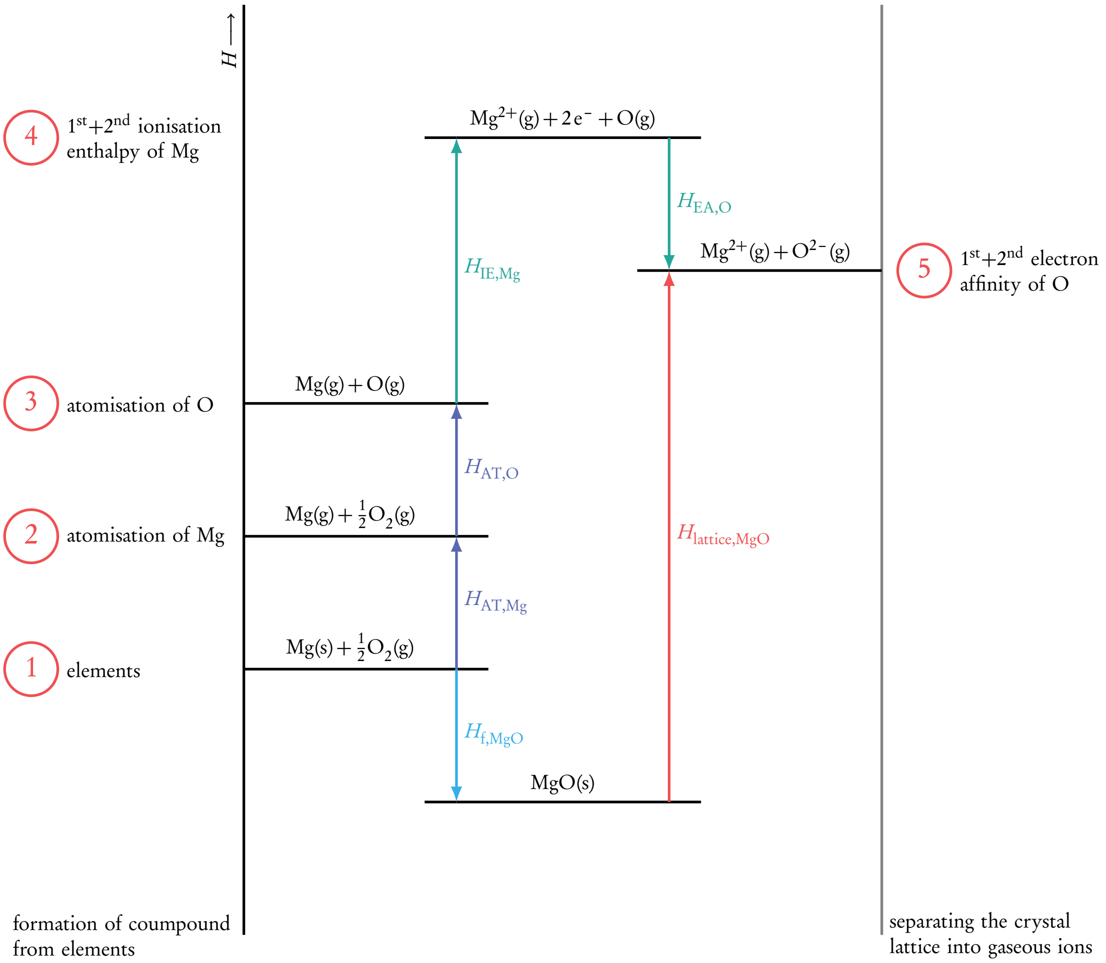
Using Hess's law: $H^{\ominus}_{\text{solution}} = H^{\ominus}_{\text{lattice}} + H^{\ominus}_{\text{hydration}}$

Born-Haber cycles

The amount of energy required to separate 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 5.6. The definition of lattice enthalpy is the enthalpy change when one mole of solid ionic compound is separated into gaseous ions: $\mathrm{MgO(s) \longrightarrow Mg^{2+}(g) + O^{2-}(g)}$.

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	$-H_{f,MgO}$	formation of elements from compound

From elements ⟶ gaseous atoms:

②	$+H_{AT,Mg}$	atomisation of Mg
③	$+H_{AT,O}$	atomisation of O

From gaseous atoms ⟶ gaseous ions:

④	$+H_{1^{st}+2^{nd}IE,Mg}$	ionisation of Mg
⑤	$+H_{1^{st}+2^{nd}EA,O}$	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*

$$\begin{aligned}\sum S_{\text{reactant}} &= 1 \times 186 + 1 \times 188.8\\ &= 375\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ \sum S_{\text{product}} &= 1 \times 197.7 + 3 \times 130.7\\ &= 590\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

4. $\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$

$$\begin{aligned}\Delta S &= \sum S_{\text{product}} - \sum S_{\text{reactant}}\\ &= 590 - 375\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ &= 215\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

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 $\Delta G_{\mathrm{f}}^{\ominus}$ 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.

$\Delta G_{\mathrm{f}}^{\ominus} = 0$ 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?

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

Substance	$S^\ominus$ / 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: $\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactant}}$

$$\Delta S = (1 \times 213.7 + 1 \times 39.8) - 1 \times 92.9$$
$$= 160.6\ \text{J K}^{-1}\ \text{mol}^{-1}$$

2. Convert to kJ K^{-1} mol^{-1} (to match ΔH)

$$= 0.1606\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

3. Write the expression for ΔG and equate it to zero.

$$\Delta G = \Delta H - T\Delta S = 0$$

4. Rearrange to calculate minimum value of T.

$$T\Delta S = \Delta H$$
$$T = \frac{\Delta H}{\Delta S}$$

Substitute ΔH and ΔS.

$$= \frac{+179}{0.1606} = 1114\ \text{K}$$

5. At T greater than the result, the reaction will be spontaneous.

The reaction will be spontaneous at $T > 1114$ K

KINETICS

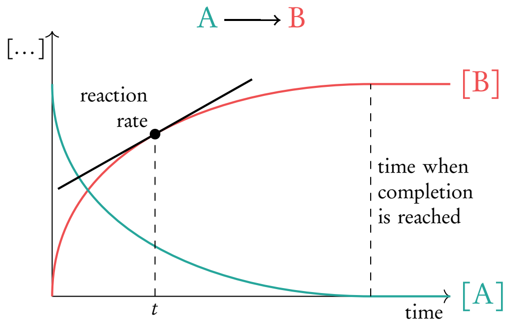
6

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

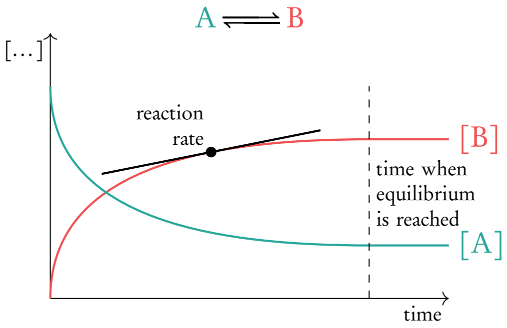
$$\text{rate} = -\frac{\Delta[\text{reactants}]}{\Delta t} = \frac{\Delta[\text{products}]}{\Delta t}$$

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 $[\mathrm{H}^+]$ or $[\mathrm{OH}-]$ 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 successful 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)

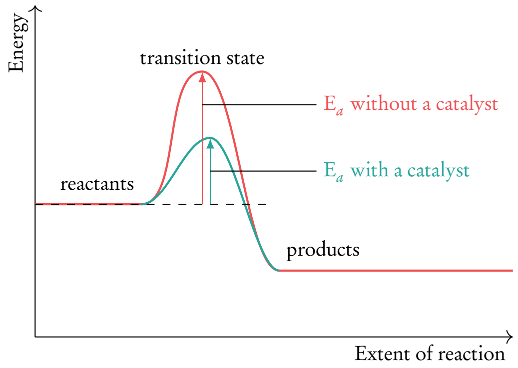
The collision theory can be used to understand how the rate of reaction can be affected. Every collision with proper orientation and with sufficient energy leads to a chemical reaction (known as **effective collisions**). When more collisions occur per second (*higher collision frequency*), there is 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.

or decrease by doing the opposite

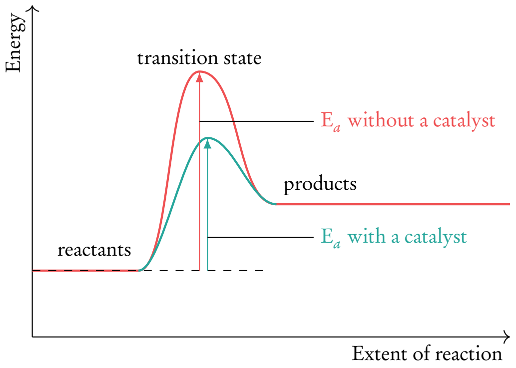
The four factors that increase the rate of reaction:

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.

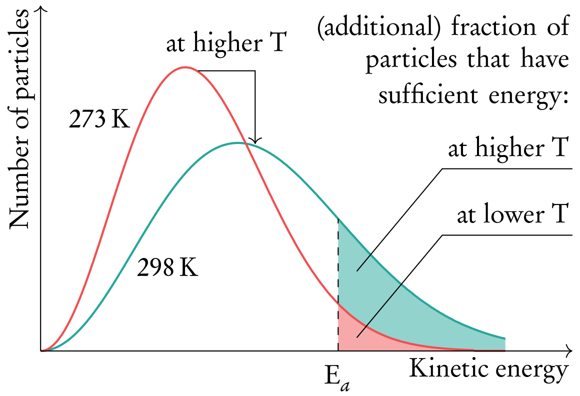
Exothermic

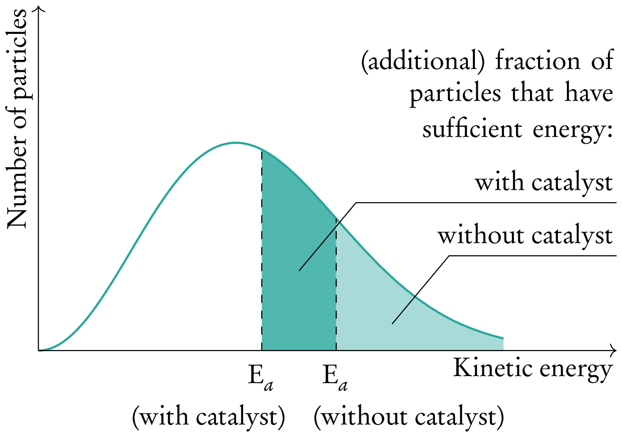


Endothermic



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: $= x + y$.

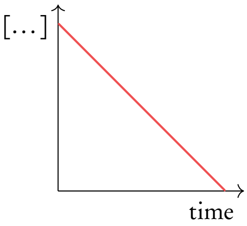
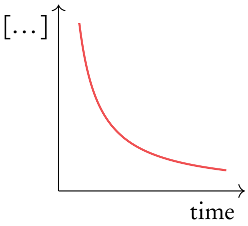
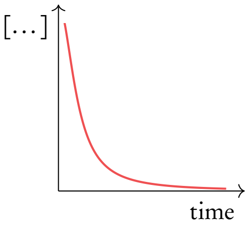
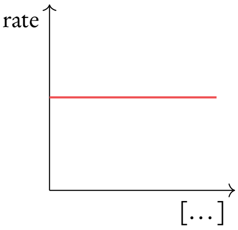
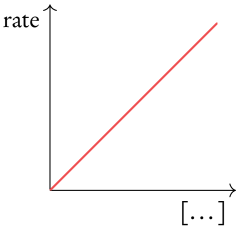
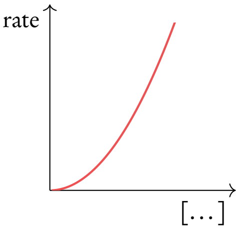
Note: the order of the reaction (and therefore also the rate equation) can *only* be derived from:

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}	$k = \text{rate}$ $= \text{mol dm}^{-3}\,\text{s}^{-1}$	$k = \frac{\text{rate}}{[\text{A}]}$ $= \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{\text{mol dm}^{-3}}$ $= \text{s}^{-1}$	$k = \frac{\text{rate}}{[\text{A}]^2}$ $= \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})^2}$ $= \text{mol}^{-1}\,\text{dm}^{3}\,\text{s}^{-1}$

*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 $k = \frac{\text{rate}}{[\text{A}]^x}$.

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.

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 $\propto [\mathrm{A}]^x$:

		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

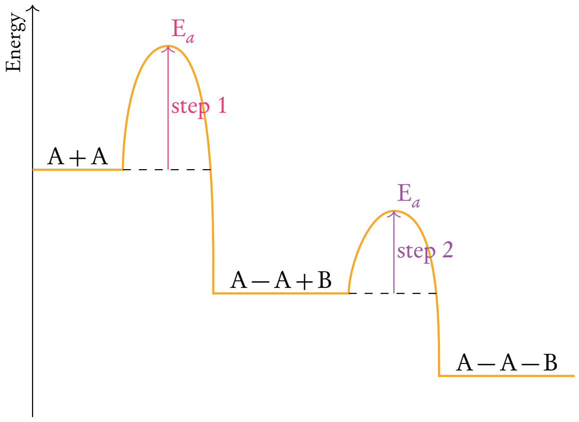
Since the collision of more than two particles with the correct orientation and sufficient energy is *extremely* unlikely, many reactions proceed in multiple steps. The step by step sequence of elementary reactions by which the overall chemical change occurs is called the reaction mechanism.

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 $2\,\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{A{-}A{-}B}$. A possible mechanism is:

step 1. $\mathrm{A} + \mathrm{A} \rightleftharpoons \mathrm{A-A}$

step 2. $\mathrm{A-A} + \mathrm{B} \longrightarrow \mathrm{A-A-B}$



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 $= k[\mathrm{A}][\mathrm{A}] = k[\mathrm{A}]^2$.

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 $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$:

step 1. $NO + NO \xrightleftharpoons{\text{fast}} N_2O_2$
step 2. $N_2O_2 + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$
step 3. $N_2O + H_2 \xrightarrow{\text{fast}} N_2 + H_2O$

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 $[8.31\,J\,K^{-1}]$
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:

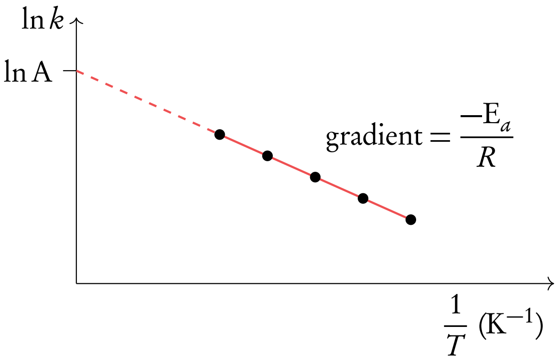
$$\begin{aligned} \ln k &= \frac{-E_a}{RT} + \ln A \\ &= \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A \\ &= m \cdot x + c \end{aligned}$$

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 extrapolation 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

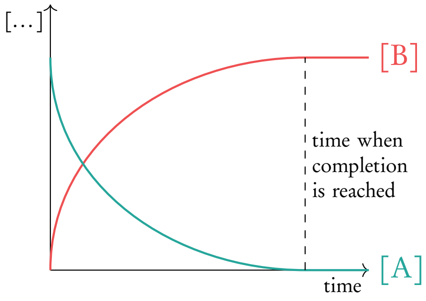
In a static equilibrium nothing changes, like for example in a mass balance. Chemical equilibriums are dynamic, there is a constant conversion in both directions such that there is no *net change*.

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

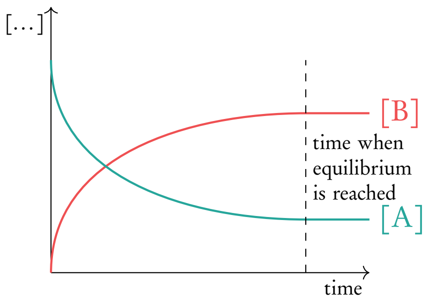
$$A \longrightarrow B$$



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 $\mathrm{A}+\mathrm{B}$ react to form $\mathrm{C}+\mathrm{D}$ and the reaction coefficients are indicated by the small letters $pqrs$.

$$p\mathrm{A} + q\mathrm{B} \rightleftharpoons r\mathrm{C} + s\mathrm{D}$$

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

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

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 $\mathrm{K_c}$ (which *only* depends on temperature).

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

Sulphur dioxide reacts with oxygen forming sulphur trioxide 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 $Q = \frac{[product]}{[reactant]}$. 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 $K_c = \frac{[products]}{[reactants]}$

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	$K_c = \frac{[N_2O_4]}{[NO_2]^2}$	$K_c{}' = \frac{[NO_2]^2}{[N_2O_4]} = \frac{1}{K_c}$

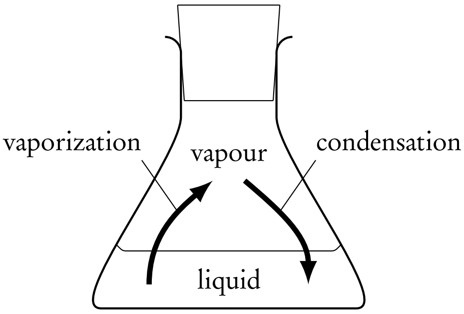
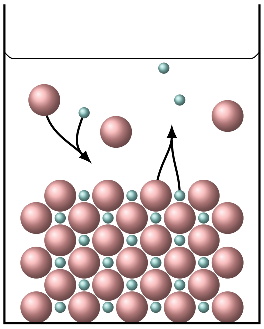
Addition: when multi-step reactions are added to give an overall reaction, the increase of a reaction coefficient cause the power in the quotient Q to increase. This means that when reactions are added, the quotients are multiplied:

$$\begin{array}{lll} \text{step 1.} & A + B \rightleftharpoons X & K_{c1} = \frac{[X]}{[A][B]} \\ \text{step 2.} & A + X \rightleftharpoons C & K_{c2} = \frac{[C]}{[A][X]} \\ \cline{2-2} \text{overall} & 2A + B \rightleftharpoons C & K_{c\text{overall}} = K_{c1} \times K_{c2} \\ & & \quad = \frac{\cancel{[X]}[C]}{[A][B][A]\cancel{[X]}} \\ & & \quad = \frac{[C]}{[A]^2[B]} \end{array}$$

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) counteract 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:

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

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 ($K_c = \dots$). The concept of limiting reactant is invalid in equilibrium reactions.

Equilibrium calculations

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

Calculate the value of the equilibrium constant K_c.

1. Convert the given values to concentrations.

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

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

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

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

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= **I**nitial+ **C**hange

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 $[\dots]_{eq}$ to calculate x and calculate all *values* in **E**quilibrium

K_c is known: insert the *expressions* from **E**quilibrium into $K_c = \dots$

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

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

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

5. Write $K_c = \dots$ and plug in the *values or expressions* of the **E**quilibrium 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

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

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.

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

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

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

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

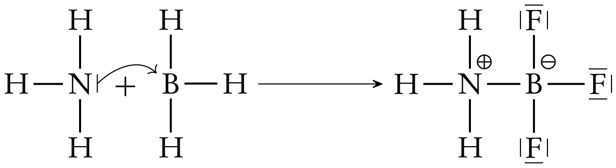
8.1 Acid and base definitions

	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	—

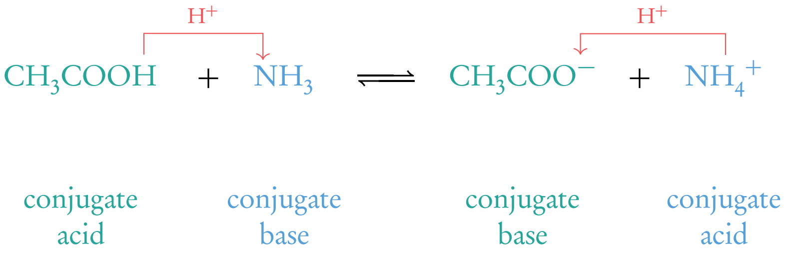
An alkali is a base that is soluble in water

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



$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

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

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

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 %

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

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

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

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

≈ 1 %

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

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, . . .

	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	

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

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…

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$
$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

Inverse to calculate […]

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}}$$
$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}}$$

Neutral solution (at 298 K pH = 7)
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^+)

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

	pH	$[\mathrm{H_3O^+}]$	$[\mathrm{OH^-}]$	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
	…	…	…	…	

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

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

8.4 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		–		–

8.5 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

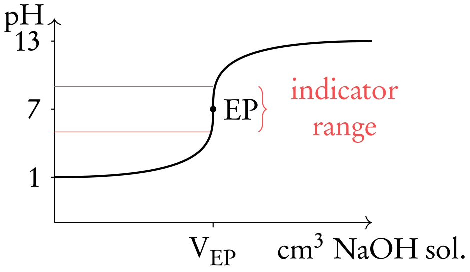
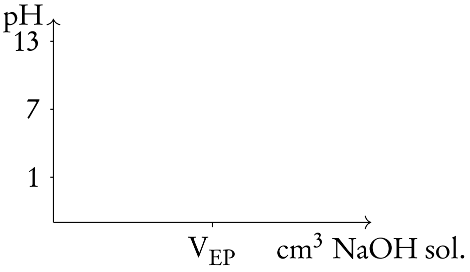
Titrant substance that reacts with the analyte, with known concentration

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 $\frac{1}{2}V_{EP}$, $pH = pK_a$

8.6 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 detrimental 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 removed leading to 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, aquatic life (fish, snails, insect larvae) is 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: $CaCO_3 + H_3O^+ \longrightarrow Ca^{2+} + CO_2 + H_2O$.

9

REDOX

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

$$\mathrm{Mg} \longrightarrow \mathrm{Mg}^{2+} + 2\,e^-$$

Mg is oxidized (loss of e^-), the oxidation state increases.

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

$$\mathrm{O_2} + 4\,e^- \longrightarrow 2\,\mathrm{O}^{2-}$$

O_2 is reduced (gain of e^-), the oxidation state decreases.

Since electrons are transferred in a redox reaction, you might think that the charges change. This is not always the case, instead the oxidation state changes:

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

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

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.

Memorize: **OIL RIG**

Oxidation
Is
Loss of electrons,

Reduction
Is
Gain of electrons

Students are often flustered that the verb ‘oxidised’ and the nouns ‘reducing agent’ / ‘reduced species’ belong together.

Just remember that OIL RIG applies to the verb and the opposites are used for the nouns ‘agent’ / ‘species’.

9.1 Oxidation states

Determine the oxidation state *per element (!)*

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

Example.

What is the oxidation number of…

… Cl in ClO_4^-?

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

So the ox. state of Cl is +7.

… C in $H_2C_2O_4$?

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

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

… P in NaH_2PO_3?

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

So the ox. state of P is +3.

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 separate 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).	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad \| \times 2$ $Cu \longrightarrow Cu^{2+} + 2e^- \quad \| \times 5$
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.

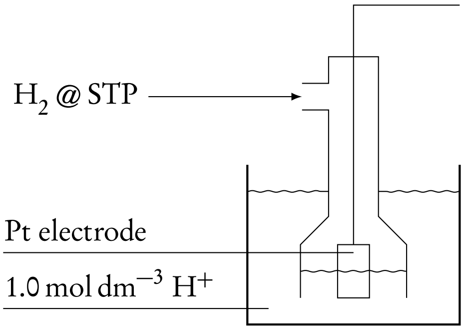
Complete the following half-reaction: $N_2H_4 \longrightarrow NO_3^-$

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 $[\dots] = 1.00\,\text{mol}\,\text{dm}^{-3}$, $p = 100\,\text{kPa}$ and $T = 298\,\text{K}$.

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



Standard electrode potential $E^\ominus{}_{\text{ox}}$ or $E^\ominus{}_{\text{red}}$ the potential of a half-reaction under standard conditions, measured against the SHE. It is a measure of the tendency of a substance to oxidise or reduce.

In DB24, all reactions are written in terms of reduction; so the greater the $E^\ominus$ value, the greater the ability to undergo reduction (and be an oxidizing agent). The $E^\ominus$ values from DB24 are only valid under standard conditions. When the conditions change, so do the $E^\ominus$ values.

For example, while under standard conditions H_2O (+1.23 V) is a stronger reduced species than Cl^- (+1.34 V). But when the Cl^- solution is concentrated, it becomes a stronger reduced species than H_2O.

When we calculate $E^\ominus$, we always do $E^\ominus_{\text{red}} - E^\ominus_{\text{ox}}$. This chapter isn't called red—ox for nothing ;-)

Standard electrode potential difference $E^\ominus$ difference between $E^\ominus_{\text{ox}}$ and $E^\ominus_{\text{red}}$

$$\begin{aligned} E^\ominus &= E^\ominus_{(\text{reduction})} &&- E^\ominus_{(\text{oxidation})} \\ &= E^\ominus_{(\text{oxidised species})} &&- E^\ominus_{(\text{reduced species})} \end{aligned}$$

By calculating $E^\ominus$, we can determine if a reaction is spontaneous (from the sign) and the voltage of an electrochemical cell.

A reaction is spontaneous when $\Delta G^\ominus$ is negative. From $\Delta G^\ominus = -nFE^\ominus$ (DB), we can derive that $\Delta G^\ominus$ is negative when $E^\ominus$ is positive, due to the − sign in the formula.

We can also easily deduce if a reaction is spontaneous from the databook: when the reduced species *is above* the oxidized species the $E^{\ominus}$ is positive and $\Delta G^{\ominus}$ is negative.

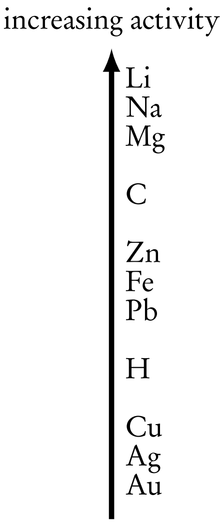
Gibbs free energy and standard electrode potential difference

The standard Gibbs free energy can be calculated from $E^{\ominus}$:

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

$\Delta G^{\ominus}$ = Gibbs free energy [kJ mol^{-1}]
n = number of e$^-$ transferred [mol]
F = Faraday's constant [9.65×10^4 C mol^{-1}]
$E^{\ominus}$ = potential difference [V]

Activity series of metals



The activity series ranks metals according to their reduction potential. Noble metals resist oxidation, while base metals readily oxidise. (A base-matal is the opposite of a noble metal, it is not a base). So Au resists oxidation, while Li promotes oxidation.

The complete activity series is shown in DB 25. Note the position of H: metals below H (such as Cu) 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 cation.

Determine the order of activity from a set of reactions.

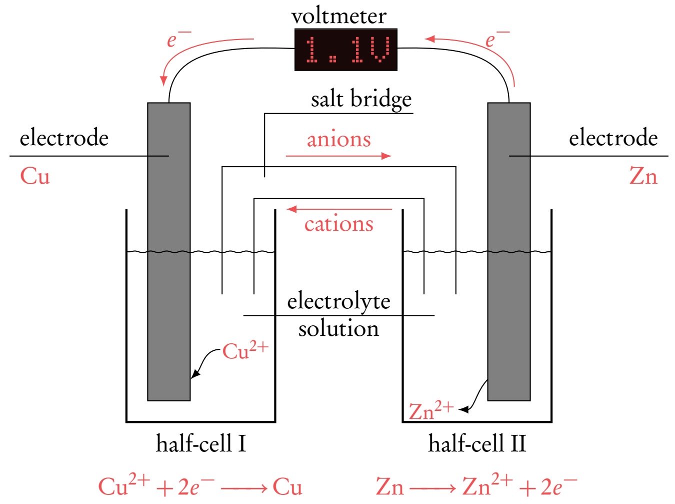
What is the correct order of reactivity of the metals X, Y and Z based on the following equations?

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

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 Electrochemical cells

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



Half-cell consists of an electrode in contact with an *electrolyte*: an aqueous solution which contains ions. A half-cell *physically* separates the red. & ox. half-reactions, and the electrons flow through the external circuit with a certain potential difference (measured in volts).

Cell diagram convention a shorthand notation for a voltaic cell, showing the substances of the different components.

Example:

$$\text{Cu} \mid \text{Cu}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$$

$$\underbrace{\text{electrode I} \mid \text{electrolyte I}}_{\text{half-cell I}} \parallel \underbrace{\text{electrode II} \mid \text{electrolyte II}}_{\text{half-cell II}}$$

Salt Bridge contains an aqueous solution of ions that move across the salt bridge to neutralize the build up of charge in both half-cells to maintain the potential difference.

To find out in which direction anions and cations flow through the salt bridge, first determine the direction of the flow of electrons (using An OIL RIG Cat).

- Cations will go in the same direction as the electrons, to neutralize the charge. So from anode to cathode through the salt bridge.
- Anions will go in the opposite direction as the electrons, to neutralize the charge. So from cathode to anode through the salt bridge.

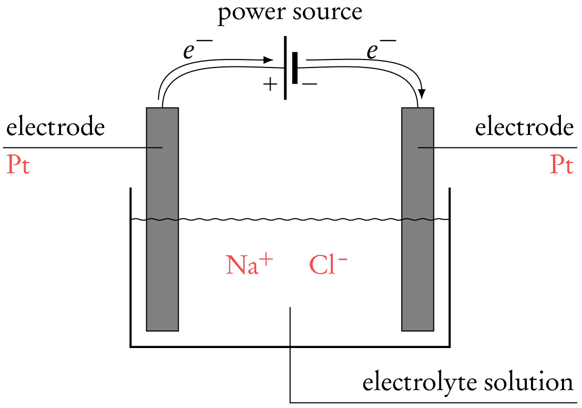
AN OIL RIG CAT

ANode
Oxidation
Is
Loss of electrons,

Reduction
Is
Gain of electrons
CAThode.

Electrolytic cell converts electrical energy to chemical energy, bringing about non-spontaneous chemical reactions.

Since the reaction is non-spontaneous, the electrolytic cell does not *need* to be physically separated into half-cells, but it may.
An electrolytic cell needs a power source, indicated with two lines: the longer is the positive terminal.



Examples of chemically inert electrodes (conductive substances that do not react) are Pt & C. They can be used in both voltaic and electrolytic cells.

Determine which half-reactions occur in an electrolytic cell.

Determine which half-reactions occur when a dilute NaCl solution is electrolysed. Find the experimental setup in the definition box above.

1.	List which particles are present at the anode (+) and cathode (—) *separately*.	**Anode** (+): Pt, H_2O, Cl^- **Cathode** (—): Pt, H_2O, Na^+
2.	Apply AN OIL RIG CAT, find the strongest reduced and oxidised species and copy the half-reactions: **Anode** (+): ox. half-reaction (reduced species) **Cathode** (—): red. half-reaction (oxidised species)	**Anode** (+): strongest oxidation $H_2O \longrightarrow \frac{1}{2}O_2 + 2\,H^+ + 2\,e^-$ **Cathode** (—): strongest reduction $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$

An important deduction from the above example can be made: O_2 is formed when water reacts at the anode, while H_2 is formed when water reacts at the cathode. You can memorize this by an extension of AN OIL… So O_2 forms at the anode!

Note that it matters whether *dilute*, *concentrated* or *molten* NaCl is electrolysed. The strongest oxidation half-reaction in each of these three cases is:

- In dilute NaCl: $H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2\,e^-$ (just like DB.24 shows).
- In concentrated NaCl: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ instead of H_2O.
- And while H_2O is present in both dilute and concentrated *solutions*, it is not when an ionic compound is in its liquid state (molten). The strongest oxidation and reduction half-reactions are: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ and $Na^+ + e^- \longrightarrow Na$.

Voltaic cell and electrolytic cells compared

AN OIL RIG CAT reminds us that *oxidation occurs at the anode*, and *reduction occurs at the cathode*. But while oxidation *always* occurs at the anode, whether the electrode is + or − depends on whether we are dealing with a voltaic cell or an electrolytic cell. Taking the voltaic cell as the standard cell, or the one you learned about first, the anode is − just like anions have negative charge. In the electrolytic cell the reverse holds.

		voltaic cell	**electrolytic cell**
ANode	Oxidation occurs here	− electrode	+ electrode
CAThode	Reduction occurs here	+ electrode	− electrode

In a voltaic cell: chemical energy is converted to electrical energy. The reaction is spontaneous, $E^\ominus$ is positive and the value = the voltage of the voltaic cell (battery).

In an electrolytic cell: electrical energy is converted to chemical energy. The reaction is not spontaneous, $E^\ominus$ is negative and the value = the minimum voltage of the power source that is required to start the reaction.

Observations and the amount of products formed

When chemical reactions occur, the amounts of reactants are reduced and the amounts of products are increased. The change in the abundance of chemicals can be linked to observations:

Colour: the colour intensity decreases if a reactant is coloured, and the color intensity increases if a product is coloured. Remember that transition metal ions are often coloured, in particular Cu^{2+} is blue.

Solid deposition: a solid can deposit onto an electrode, changing the appearance and increasing the mass.

Gas discharge in a solution: bubbles form when a gas is formed in solution. In particular: O_2 can form at the anode and H_2 at the cathode, given that H_2O reacts at the anode or cathode respectively.

pH: the pH changes when the concentrations of H_3O^+ or OH^- change, which can be measured.

The mole amounts of reactants / products in an electrolytic cell depend on three factors:

1. Current (amount of electrons that pass through the cell per second)
2. Duration (the longer, the more electrons pass through the cell)
3. Charge on the ion (the higher, the more electrons required to make a neutral atom)

Electroplating

The process of using electrolysis to deposit a metal on top of a conductive object that must satisfy three conditions.

1. Electrolyte must contain ions of the metal to be deposited
2. Cathode is made of the object that will be plated/coated (conductive)
3. Anode can also be made of the metal that will be deposited to refill the ions in the electrolyte

Calculate the amount that reacts/forms in an electrolytic cell.

Calculate the mass of copper that is deposited on the cathode during the electrolysis of a $CuCl_2$ solution with a current of 5.0 A for 30 minutes.

1.	Write the half-reaction that occurs.	$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
2.	Calculate number of moles of e^-: $n(e^-) = \frac{\text{current (A)} \times \text{time (s)}}{\text{Faraday's constant (F)}}$ Note: this formula is not in the DB.	$n(\text{mol})e^- = \frac{5.0\,\text{A} \times 30\,\text{min} \times 60\,\text{s}\,\text{min}^{-1}}{9.65 \times 10^4}$ $= 9.3 \times 10^{-2}$ mol of electrons
3.	Use the mole ratio from the half-reaction to calculate moles of the desired substance.	Since the mole ratio $Cu(s) : e^- = 1 : 2$, $n\ (Cu(s)) = \frac{9.3 \times 10^{-2}\,\text{mol}}{2} =$ 4.7×10^{-2} mol $Cu(s)$
4.	Convert to the required units.	m = n × Mm $m = 4.7 \times 10^{-2}\,\text{mol} \times 63.55\,\text{g}\,\text{mol}^{-1}$ $= 3.0\,\text{g}\ Cu(s)$

9.5 The Winkler method and the BOD

Winkler method two sequential titrations that are performed on surface water to measure the initial amount of dissolved oxygen, and the amount after some pre-defined time to determine the BOD.

Biochemical Oxygen Demand (BOD) the amount of oxygen used to decompose organic matter in a sample of water over a specified time period.

If there is much organic matter (bad), much oxygen will be used up by bacteria during decomposition. And if there is little dissolved oxygen to begin with (bad), aquatic life will struggle to survive.

Thermal Pollution: water used in cooling engines in factories tend to be released into a water system, which decreases the dissolved oxygen content.

Organic Matter: a greater amount of organic matter in water means more micro-organisms will be present, thus decreasing the dissolved oxygen content. This usually occurs due to *eutrophication*: the excess use of fertilizers and detergents increases the amount of 'food' for bacteria and algea, increasing the BOD.

The Winkler determination of BOD is based on a sequence of redox reactions. The mole ratio between $O_2(aq)$ = dissolved oxygen (analyte) : $S_2O_3{}^{2-}$ (titrant) = 1:4.

ORGANIC CHEMISTRY

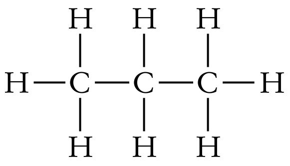
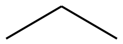
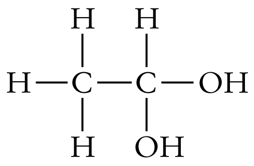
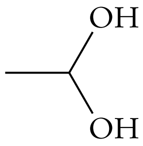
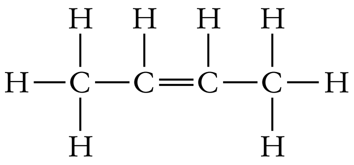
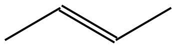
10

10.1 Fundamentals of organic chemistry

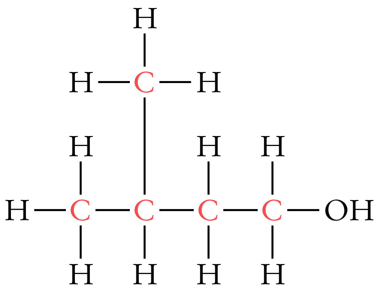
Empirical formula shows the simplest whole number ratio of atoms in a compound.

Molecular formula shows the actual number of atoms in a molecule.

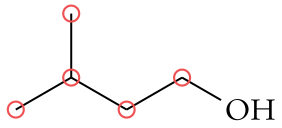
Structural formula shows the bonds between atoms, that form a molecule. It can be shown in full, condensed and skeletal form.

structural formulas			molecular formula	empirical formula
full	**condensed**	**skeletal**		
	$CH_3CH_2CH_3$		C_3H_8	C_3H_8
	$CH_3CH(OH)_2$		$C_2H_6O_2$	CH_3O
	$CH_3CHCHCH_3$		C_4H_8	CH_2

A note on skeletal structures: the C-atoms are not explicitly drawn, but a C-atom with the correct number of H-atoms is implied at the start/end of a line, and where lines intersect.



is the same as



Homologous series succesive members differ from each other by $-CH_2-$.

alkane homologous series

name	structure	BP
methane	CH_4	−162 °C
ethane	CH_3CH_3	−89 °C
propane	$CH_3CH_2CH_3$	−42 °C
butane	$CH_3CH_2CH_2CH_3$	0 °C
pentane	$CH_3CH_2CH_2CH_2CH_3$	36 °C

alcohol homologous series

name	structure	BP
methanol	CH_3OH	64 °C
ethanol	CH_3CH_2OH	78 °C
propan-1-ol	$CH_3CH_2CH_2OH$	98 °C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	118 °C
pentan-1-ol	$CH_3CH_2CH_2CH_2CH_2OH$	138 °C

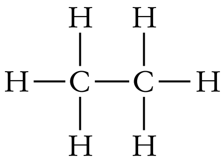
Members of a homologous series have *similar chemical properties* (since they share the same functional group) and they show a *gradual change in physical properties* (for example their melting-/boiling points increase as a result of increasingly stronger London dispersion forces).

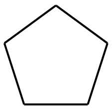
10.1.1 Classification of hydrocarbons

Hydrocarbons are compounds containing only hydrogen and carbon atoms.

Saturated hydrocarbons

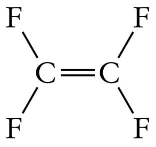
contain only C—C (alkane)





Unsaturated hydrocarbons

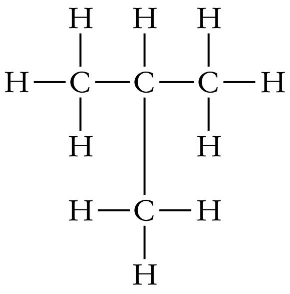
contains C=C (alkene) or C≡C (alkyne)

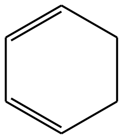


$H-C\equiv C-H$

Aliphatic compounds

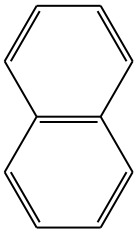
compounds without benzene rings

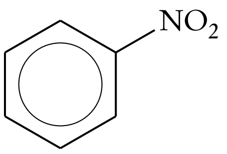




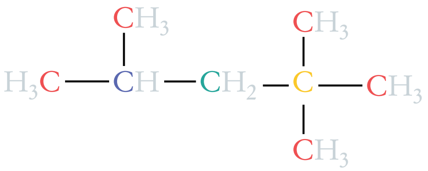
Aromatic compounds

compounds with at least one benzene ring





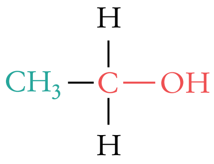
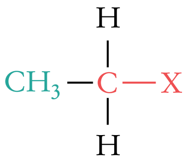
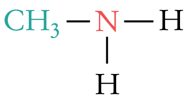
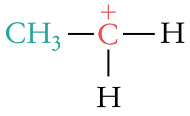
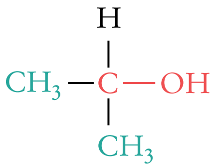
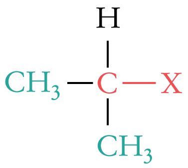
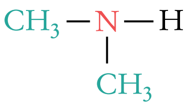
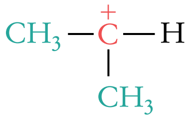
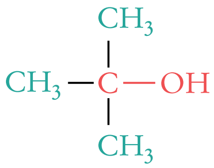
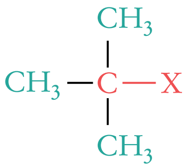
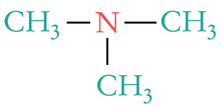
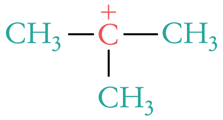
Number of C neighbours



$H_3C-\overset{CH_3}{CH}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

primary	1°	directly bonded to one C atom
secondary	2°	directly bonded to two C atoms
tertiary	3°	directly bonded to three C atoms
quaternary	4°	directly bonded to four C atoms

Alcohols, halogenoalkanes, amines and carbocations can be primary (1°), secondary (2°) or tertiary (3°). The atom of interest is the C atom that is bonded to —OH or —X or that carries the positive charge. For amines it is different, the atom of interest is the N atom.

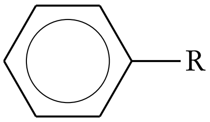
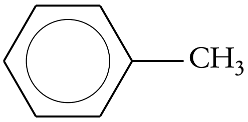
	alcohol	halogenoalkane	amine	carbocation
primary (1°)	 $CH_3-\overset{H}{\underset{H}{C}}-OH$	 $CH_3-\overset{H}{\underset{H}{C}}-X$	 $CH_3-\underset{H}{N}-H$	 $CH_3-\overset{+}{\underset{H}{C}}-H$
secondary (2°)	 $CH_3-\overset{H}{\underset{CH_3}{C}}-OH$	 $CH_3-\overset{H}{\underset{CH_3}{C}}-X$	 $CH_3-\underset{CH_3}{N}-H$	 $CH_3-\overset{+}{\underset{CH_3}{C}}-H$
tertiary (3°)	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-X$	 $CH_3-\underset{CH_3}{N}-CH_3$	 $CH_3-\overset{+}{\underset{CH_3}{C}}-CH_3$

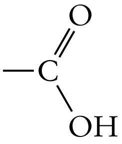
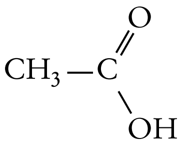
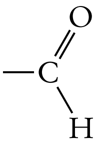
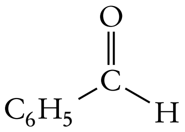
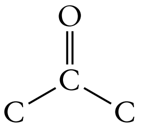
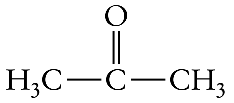
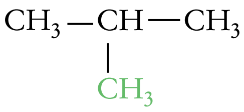
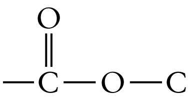
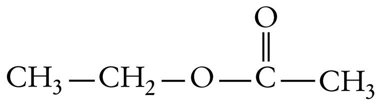
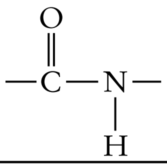
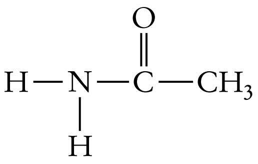
10.1.2 Functional groups

Chemical class a family of compounds that share the same functional group.

Functional group gives distinct chemical properties to a compounds, the reactive part of the molecule.

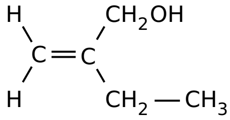
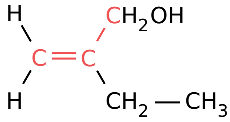
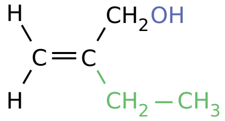
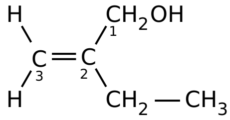
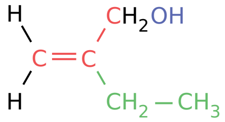
Sometimes the class of compounds has a different name as the functional group. The functional group names have come up quite often on IB-exams, be sure you know their names.

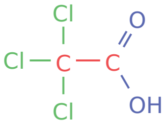
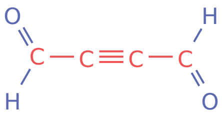
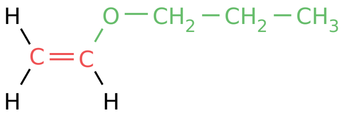
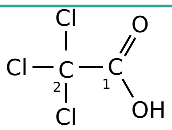
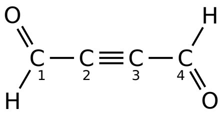
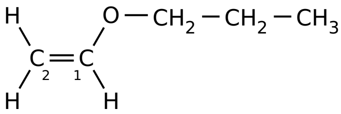
chemical class	functional group	contains	root	examples
alkane	alkyl	C—C only	alkane	$CH_3-CH_2-CH_3$
alkene	alkenyl	C═C	alkene	$CH_2{=}CH-CH_3$
alkyne	alkynyl	C≡C	alkyne	$H-C\equiv C-H$
arene (benzene derivative)	phenyl			

chemical class	functional group	condensed	full structural	suffix/prefix	examples
carboxylic acid	carboxyl	$-COOH$		-oic acid	
aldehyde	aldehyde	$-CHO$		-al	
ketone	carbonyl	$-CO-$		-one	 $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$
alcohol	hydroxyl	$-OH$		-ol	CH_3-OH
amine	amine	$-N(H,R)_2$		-amine	H_2N-CH_3
nitrile	nitrile	$-CN$	$-C\equiv N$		$N\equiv C-CH_3$
ether	alkoxy	$-O-$	$C-O-C$	alkoxy-	CH_3-O-CH_3
halogen		$-X$		halogeno-	CH_3-Br
side-chain		$-CH_3$, $-CH_2CH_3\ldots$		alkyl-	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH_3$
ester	ester	$-COO-$	 $-\overset{O}{\overset{\|}{C}}-O-C$		 $CH_3-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$
amide	carboxamide	$-CON(H,R)_2$	 $-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{\vert}{N}}-$		 $H-\underset{H}{\underset{\vert}{N}}-\overset{O}{\overset{\|}{C}}-CH_3$

10.1.3 Nomenclature

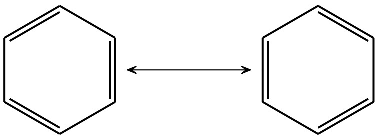
Naming organic molecules

	Determine the name of the following compound:		
1.	Determine the longest uninterrupted chain, including the functional group(s) **alk:** meth-, eth-, prop-, but-, pent-, hex- **types:** -ane, -ene, -yne		**root:** propene the longest chain with the —OH and C=C included is three, not four.
2.	Determine the functional groups **suffix:** -oic acid, -al, -one, -ol, -amine **prefix:** halogeno-, alkoxy-, alkyl- **multiple:** di-, tri-, tetra-. . . etc		suffix: -ol prefix: -ethyl
3.	Number as low lowest possible: 1 C-atom with the functional group 2 double and triple bonds 3 other		start counting so that the functional group —OH is lowest.
4.	Write full name: prefixrootsuffix 1 dash (-) between numbers and letters 2 comma (,) between numbers		2-ethylprop-2-ene-1-ol

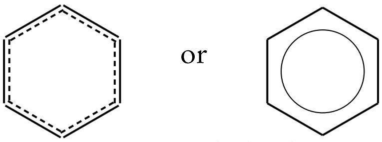
			
1.	root: ethane	root: butyne	root: ethene
2.	suffix: -oic acid prefix: trichloro-	suffix: -dial prefix: —	suffix: — prefix: propoxy-
3.			
4.	2,2,2-trichloroethanoic acid	but-2-yne-1,4-dial	1-propoxyethene

10.1.4 Resonance structure of benzene

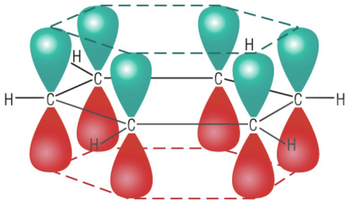
The simplest aromatic hydrocarbon is benzene, C_6H_6.



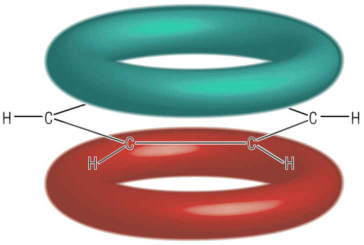
resonance structures



resonance hybrid

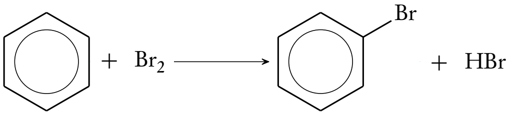


The p orbitals on the sp^2 hybridized C atoms overlap sideways above & below the molecule, resulting in a ring of delocalised π electrons.



The six $\mathrm{C\overset{\cdots}{-}C}$ are each equally strong and long (bond order is 1.5), instead of having three $\mathrm{C{-}C}$ and three $\mathrm{C{=}C}$ bonds (of bond orders 1 and 2). The strength and length of the $\mathrm{C\overset{\cdots}{-}C}$ bonds are somewhere between that of $\mathrm{C{-}C}$ and $\mathrm{C{=}C}$.

Chemical proof: while regular alkenes readily undergo addition reactions, benzene resists addition and instead undergoes substitution reactions.

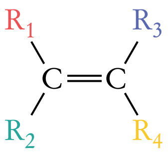
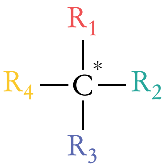
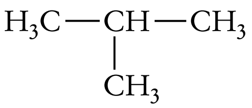
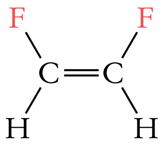
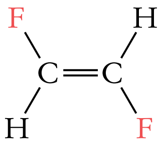
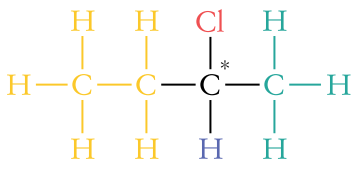
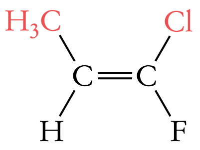
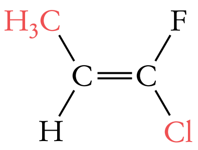
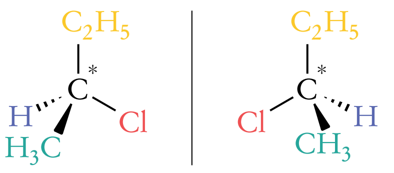


Physical proof: the following table shows measured bond strengths and lengths.

	bond strength in kJ $\mathrm{mol^{-1}}$	bond length in nm
$\mathrm{C{-}C}$	346	0.154
$\mathrm{C{=}C}$	614	0.134
$\mathrm{C\overset{\cdots}{-}C}$	507	0.140

10.2 Isomers

Isomers	are molecules that have something in common, but are different.
Stereoisomers	have different spatial arrangements (→ both cis/trans and optical isomers).
Chiral atom	contains 4 different groups → optical isomers.

structural isomers	cis/trans and E/Z	optical isomers
same molecular formula, but different structural formula	different spatial arrangement of atoms around C=C or ring due to lack of free rotation	different spatial arrangement of four different groups on a chiral C-atom
		
requirement		
	$R_1 \neq R_2$ and $R_3 \neq R_4$	$R_1 \neq R_2 \neq R_3 \neq R_4$
examples		
C_4H_{10}	cis/trans	chiral atom/centre
$H_3C-CH_3-CH_3-CH_3$  $H_3C-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_3$	 cis: same  trans: opposite	
C_2H_6O	E/Z	drawing isomers
H_3C-CH_2-OH $H_3C-O-CH_3$	 Z: same  E: opposite	 mirror
chemical & physical properties		
(very) different/distinct and can (easily) be separated	similar, but dipole moment may be different	all chemical and physical properties are the same; except the rotation of plane polarized light and reactions with enzymes

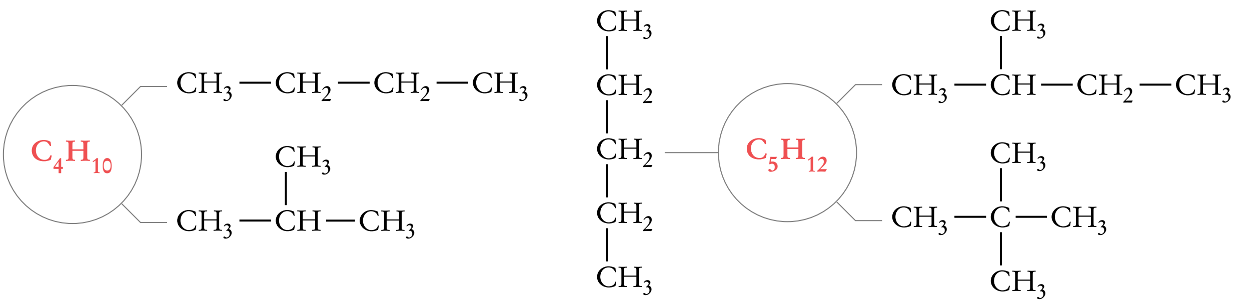
10.2.1 Structural isomers

Structural isomers same molecular formula, different structural formulas

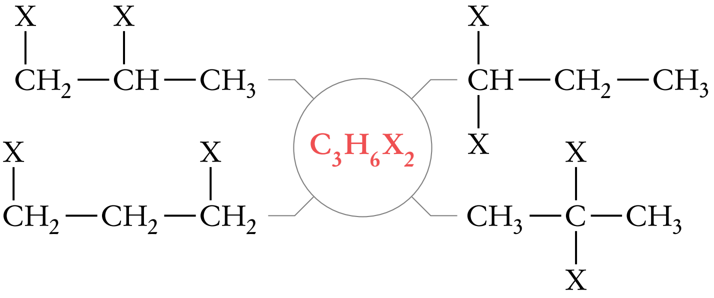
There are three sub-categories of structural isomers, that correspond to three strategies when drawing structural isomers:

Generally speaking, branched isomers exist when molecules have 4 or more C-atoms

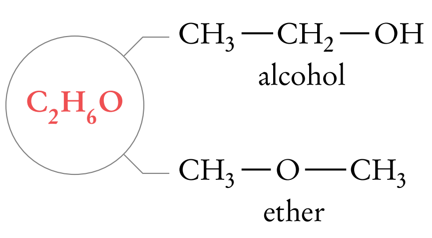
1. chain isomers: arise because of the possibility of branching in carbon chains.

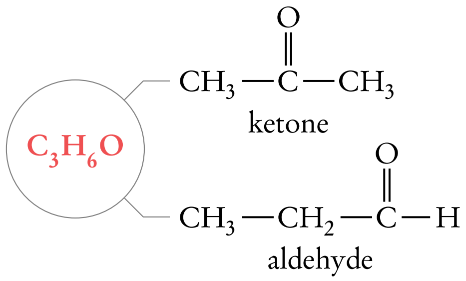


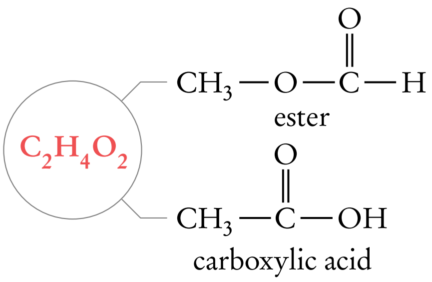
2. positional isomers: the carbon skeleton remains unchanged, but groups have different positions.

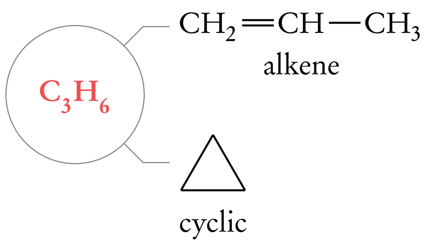


3. functional group isomers: the isomers contain different functional groups.different positions.





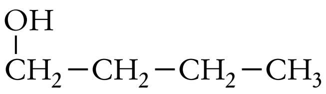
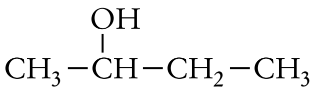
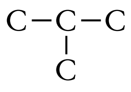
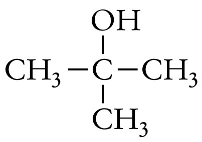
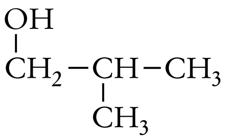
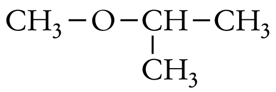




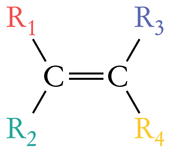
When you are asked to draw the structural isomers from a given molecular formula, think about *all three* types. Ask yourself: Can you branch the carbon chain? Can you move a group around on that chain? Is it possible to change the functional group?

Finding structural isomers

Find all the structural isomers that exist of $C_4H_{10}O$.

1. **Branches:** Is branching a possibility?	2. **Positions:** Draw any one isomer. If any, can the position of the functional group be drawn at a different position?	3. **Functional group:** Can you draw another functional group instead of the previous? Also change the position of this group.
$C-C-C-C$	 $\overset{\overset{OH}{\vert}}{CH_2}-CH_2-CH_2-CH_3$  $CH_3-\overset{\overset{OH}{\vert}}{CH}-CH_2-CH_3$	$CH_3-CH_2-O-CH_2-CH_3$ $CH_3-O-CH_2-CH_2-CH_3$
 $C-\underset{\underset{C}{\vert}}{C}-C$	 $CH_3-\overset{\overset{OH}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-CH_3$  $\overset{\overset{OH}{\vert}}{CH_2}-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$	 $CH_3-O-\underset{\underset{CH_3}{\vert}}{CH}-CH_3$

10.2.2 cis/trans and E/Z isomers



geometric isomers synonym for cis/trans and E/Z. This occurs when rotation in a molecule is restricted due to a double bond (or a ring).

There are no geometric isomers if $R_1 = R_2$ or $R_3 = R_4$.

cis/trans isomers when two groups are identical, those can be on the same side (cis) or on the opposite side (trans). Otherwise → E/Z.

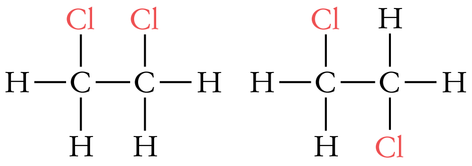
CIP priority rule atoms with larger molar mass receive higher priority.

1. Compare the mass of the first atom.
2. If they are the same, compare the masses of the next atom etc.

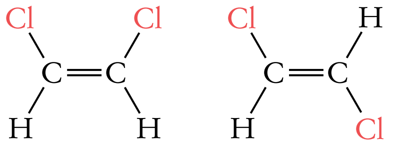
E/Z isomers when all the four R-groups are all different, use CIP to determine whether the groups with highest priority are on the zame side (Zusammen = together) or on the opposite side (Entgegen = opposite)

cis/trans isomers

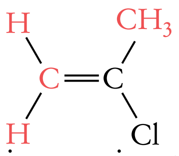
Since internal rotation is limited around a double bond, molecules that have groups on the same side (*cis*) of the double bond are different from molecules with those groups on opposite sides (*trans*) of the double bond.



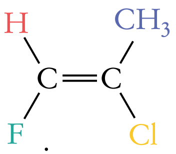
molecules are *the same* since the C—C bond allows rotation.



“cis” “trans”
molecules are *not the same* since the C=C bond does not allow free rotation.

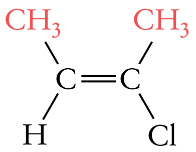


no cis/trans isomers since the left C has two identical groups.

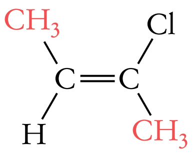


cannot assign cis or trans since no two groups are the same → E/Z

E/Z isomers



trans-2-chloro-2-butene
Z-2-chloro-2-butene



cis-2-chloro-2-butene
E-2-chloro-2-butene

It appears that *cis* (on the same side) and Zusammen (together) mean the same thing, but they do not! The rules to determine which is which differ; for *cis/trans* we look at the positions of the same groups over the double bond and for *E/Z* we look at the positions of the groups with highest CIP priority over the double bond.

To determine the name using the *E/Z* system, look at each C in the C=C separately and assign a priority (1 or 2) to both groups attached to each of the C's. In the above molecule we should assign priority as follows:

10.2.3 Optical isomers

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10.3 Reactions

10.3.1 Combustion

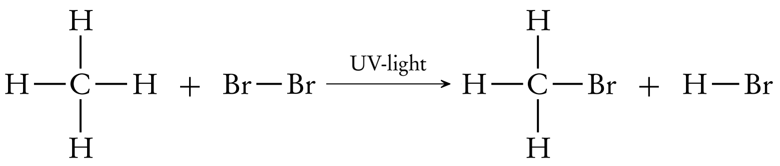
Combustion is an exothermic reaction between a fuel and oxygen. Based on the elemental composition of a fuel, we can predict which products form after combustion.

element in fuel	combustion product	averse effects
H	H_2O	–
C	CO_2 (complete)	greenhouse gas
	CO (incomplete)	poisonous, irreversibly binds to haemoglobin
	C (incomplete)	irritation to the repository tract
S	SO_2	acid deposition
N	NO	acid deposition

Dependent if oxygen is in excess or limited, *complete combustion* (→ CO_2) or *incomplete combustion* (→ CO and/or C) occurs.

10.3.2 Substitution

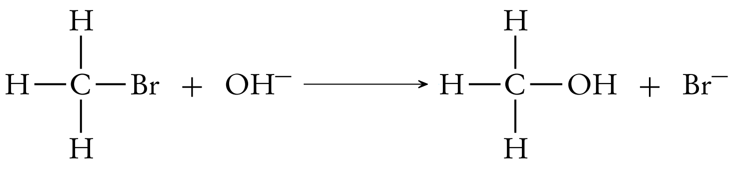
Free radical substitution reaction a halogen atom (—X) replaces a hydrogen atom (—H) in *alkanes*, under the influence of light.



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H + Br-Br \xrightarrow{\text{UV-light}} H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Br + H-Br$$

Alkanes have strong non-polar C—C and C—H bonds, hence alkanes are relatively inert (unreactive). Under the influence of (UV-)light, halogens (X_2) can form very reactive radicals that can replace H-atoms in alkanes.

Nucleophilic substitution reaction a ‘stronger’ nucleophile such as OH^- replaces a ‘weaker’ nucleophile such as —X

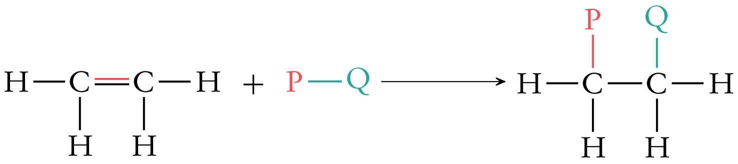


$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-Br + OH^- \longrightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH + Br^-$$

Halogenoalkanes are more reactive than alkanes since they possess polar bonds $\overset{\delta+}{C}-\overset{\delta-}{X}$. The $\overset{\delta+}{C}$-atom can be ‘attacked’ by electron-rich nucleophiles. Moreover, C—X bonds are typically weaker than C—H bonds making —X easier to replace. Since halogenoalkanes are more reactive than alkanes, no light is required to initiate the reaction.

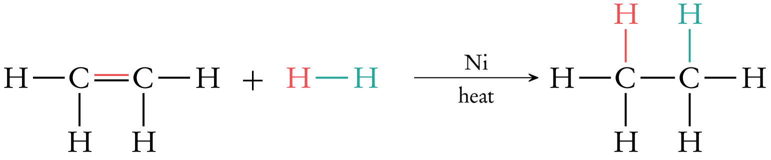
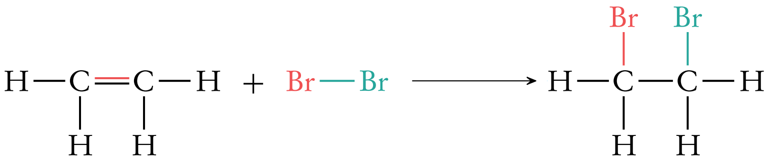
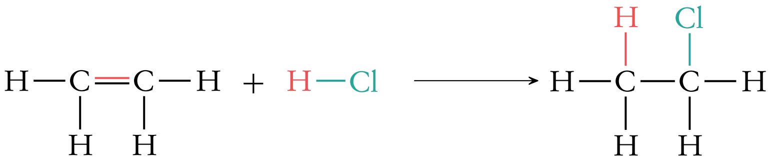
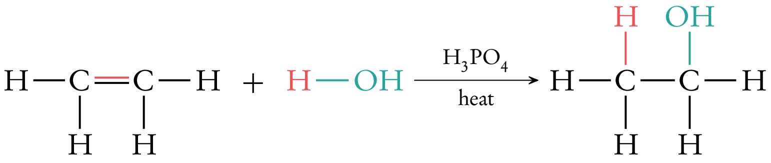
10.3.3 Addition

Addition reaction the π bond in *alkenes* or *alkynes* opens, and new bonds form to each of the two carbons around the original π bond.



$$\mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H + P{-}Q \longrightarrow H{-}\overset{P}{\underset{H}{C}}{-}\overset{Q}{\underset{H}{C}}{-}H}$$

π bonds are somewhat weaker than σ bonds, so alkenes and alkynes are more reactive than alkanes resulting in the fact that no light is needed for reaction. Alkenes and alkynes will undergo addition reactions instead of substitution.

	addition of	example
hydrogenation → alkane	$\mathrm{H{-}H}$	 $\mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H + H{-}H \xrightarrow[heat]{Ni} H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$
halogenation → dihalogeno	$\mathrm{X{-}X}$	 $\mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H + Br{-}Br \longrightarrow H{-}\overset{Br}{\underset{H}{C}}{-}\overset{Br}{\underset{H}{C}}{-}H}$
halogenation → halogeno	$\mathrm{H{-}X}$	 $\mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H + H{-}Cl \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}\overset{Cl}{\underset{H}{C}}{-}H}$
hydration → alcohol	$\mathrm{H{-}OH}$	 $\mathrm{H{-}\underset{H}{C}{=}\underset{H}{C}{-}H + H{-}OH \xrightarrow[heat]{H_3PO_4} H{-}\overset{H}{\underset{H}{C}}{-}\overset{OH}{\underset{H}{C}}{-}H}$

Differentiate experimentally between alkanes and alkenes/alkynes

Br_2 has a distinct brown colour. By adding a drop to an excess alkane or alkene/alkyne, the brown colour completely disappears as Br_2 is the limiting reactant:

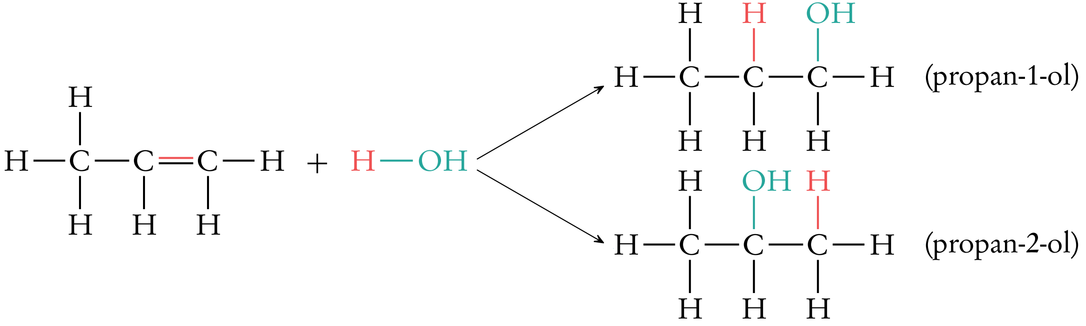
substitution $\mathrm{CH_3{-}CH_3 + Br_2 \xrightarrow{light} CH_3{-}CH_2Br + HBr}$

addition $\mathrm{CH_2{=}CH_2 + Br_2 \longrightarrow CH_2Br{-}CH_2Br}$

Performing the experiment in the dark however, prevents the substitution reaction from occuring: the Br_2 would only decolorize if the addition reaction can occur, thus providing evidence for the presence of double bonds.

Asymmetric addition

When an asymmetric alkene (such as propene $CH_2{=}CH{-}CH_3$) reacts with an asymmetric reactant (such as H—X or H—OH), two structural isomers are formed from two different competing reactions.



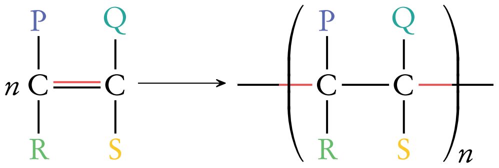
Addition polymerization

Polymer a large molecule that forms by linking many monomers together. Synthetic plastics are an example of polymers.

Addition polymer the monomers react by breaking the double bond, linking on every second C atom.

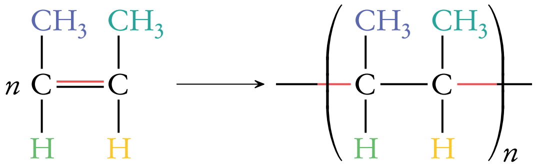
The trick to drawing polymers is to draw 90° angles in the monomers:

in general:



Example.

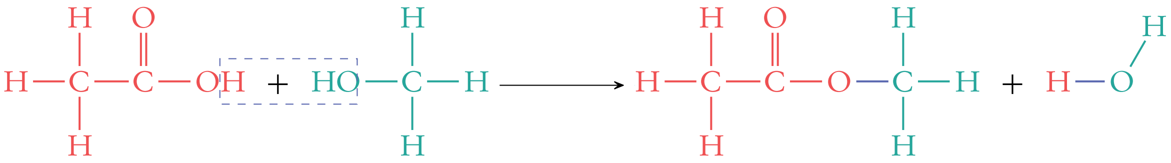
polybut-2-ene:



The repeating unit of an addition polymer always contains *two* C atoms, since it reflects the structure of the monomer. Reasoning backwards starting from the polymer, it is between these two C atoms that the monomer had the double bond.

10.3.4 Condensation / esterification reaction

Esterification carboxylic acid + alcohol $\xrightarrow[\text{heat}]{H_2SO_4}$ ester + H_2O



ethanoic acid

methanol

methylethanoate

Naming esters is different from naming other organic compounds. The general name of esters is alkylalkanoate, where the alkyl part of the name is derived from the alcohol parent and alkanoate is derived from the carboxylic acid parent molecule.

methyl is derived from the alcohol, methanol

methyl ethanoate

ethan signifies two carbons in the acid, -oate is the ester suffix

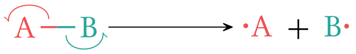
Remember that “alk” in both parts of the name should be replaced by the numeric prefix meth-, eth-. . . to signify the number of C atoms.

10.4 Reaction mechanisms

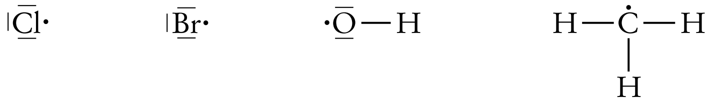
10.4.1 Definitions and understandings

Reaction mechanism reactions take place gradually or in steps; breaking bonds and forming new bonds. Reaction mechanisms show the movement of single electons with 'fishhook' arrows ($\rightharpoonup$) or the movement of electron pairs with regular arrows ($\longrightarrow$) for each step.

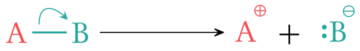
Homolytic fission the process of breaking a covalent bond where each of the fragments retain one of the bonding electrons, forming radicals.



Free radical contains an unpaired electron indicated by a dot, a reactive species formed when a molecule undergoes homolytic fission.



Heterolytic fission the process of breaking a covalent bond where one fragment takes both bonding electrons from the other.

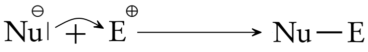


A nucleophile is a Lewis base, an electrophile is a lewis acid.

Nucleophile electron rich species capable of donating an electron pair to form a covalent bond. The donated electon pair is usually a lone pair, but it can also be the π electron pair in a double or triple bond.

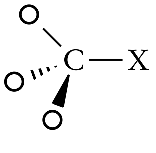
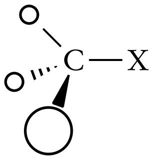
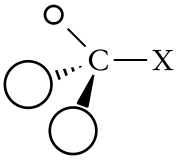
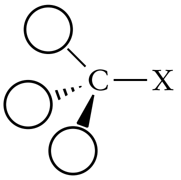
Electrophile electron deficient species capable of accepting an electron pair to form a covalent bond. Usually an ion with a $+$ charge, or any atom with a δ^+ charge.

Notes on drawing arrows the base of an arrow always starts from an electron pair (lone or bonding pair) and always points to an atom. Also, arrows never pass a reaction arrow.



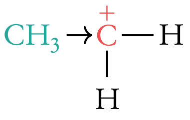
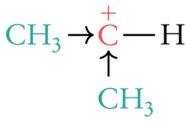
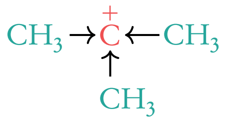
Steric hindrance is the obstruction in 3d space by bulky groups, preventing successful collision or making the successful collision between reactants less likely, thus slowing down reactions.

The following table shows that approach from the left becomes increasingly more difficult due to the greater number of bulkier groups. —H atoms are small so they are drawn as a small circle, while alkyl groups such as $-CH_3$ are bulkier and will be drawn as a larger circle.

methane	1° halogeno-alkane	2° halogeno-alkane	3° halogeno-alkane
			
least steric hindrance	→		most steric hindrance

Positive inductive effect alkyl groups (such as $-CH_3$, $-C_2H_5$…) donate electron density, thereby reducing the positive charge on the carbocation, thus stabalising a carbocation. The more alkyl groups that are attached to a carbocation, the more electron density the carbocation receives and so the more stable it becomes.

Generally the more stable a compound is, the easier it is to form. So when a carbocation is more stable, the activation energy goes down and with it the rate of its formation goes up.

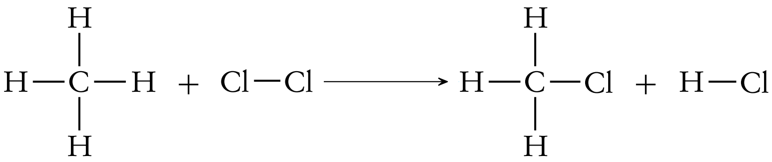
1° carbocation	2° carbocation	3° carbocation
 $CH_3\rightarrow\overset{+}{\underset{\underset{H}{\mid}}{C}}-H$	 $CH_3\rightarrow\overset{+}{\underset{\underset{CH_3}{\uparrow}}{C}}-H$	 $CH_3\rightarrow\overset{+}{\underset{\underset{CH_3}{\uparrow}}{C}}\leftarrow CH_3$
least stable carbocation	→	most stable carbocation

The arrows show the pushing of electron density by alkyl groups to the carbocation, not dative/coordinate covalent bonds.

Carbocation species are highly reactive electrophilic intermediates (C *really* prefers having 4 bonds instead of 3): the formation of carbocation intermediates is always rate determining, the subsequent reaction step will always rapidly form a covalent bond from a lone-pair on a nucleophile to the carbocation.

10.4.2 Free radical substitution

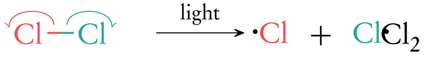
Free radical substitution reaction a halogen atom (—X) replaces a hydrogen atom (—H) in *alkanes*, under the influence of light. The mechanism proceeds in three stages: initiation, propagation and termination.



$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

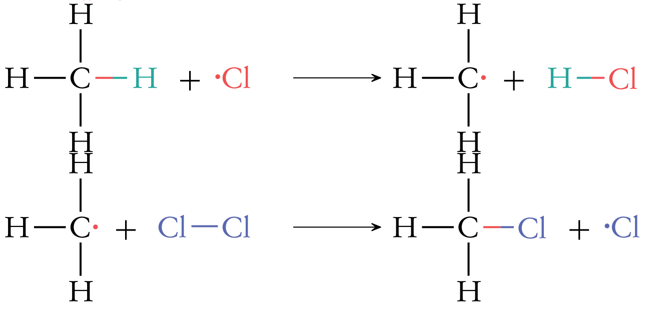
The free radical substitution reaction of CH_4 with Cl_2 (above) is depicted below, on the left the reaction in full structural formulas and the identical reactions on the right in condensed structural formulas:

1. **Initiation:** produces two radicals from X–X



$$\xrightarrow{\text{light}} 2Cl\cdot$$

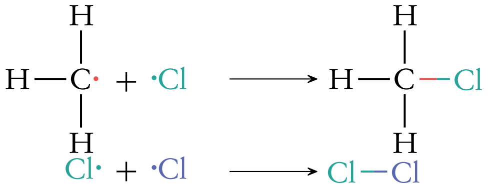
2. **Propagation:** the number of radicals in the reaction mixture does not change.



$$CH_4 + Cl\cdot \longrightarrow CH_3\cdot + HCl$$

$$CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

3. **Termination:** two radicals combine to form new molecules.

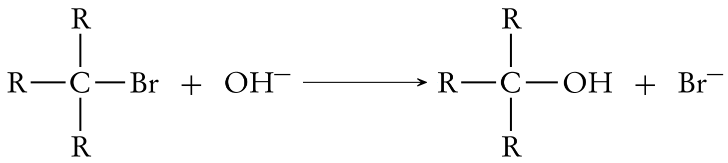


$$CH_3\cdot + Cl\cdot \longrightarrow CH_3Cl$$

$$2Cl\cdot \longrightarrow Cl_2$$

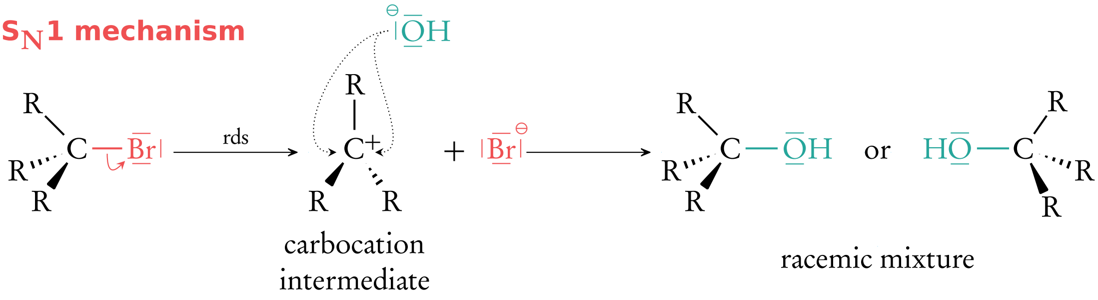
10.4.3 Nucleophilic substitution

Nucleophilic substitution reaction a ‘stronger’ nucleophile such as OH^- replaces a ‘weaker’ nucleophile such as —X

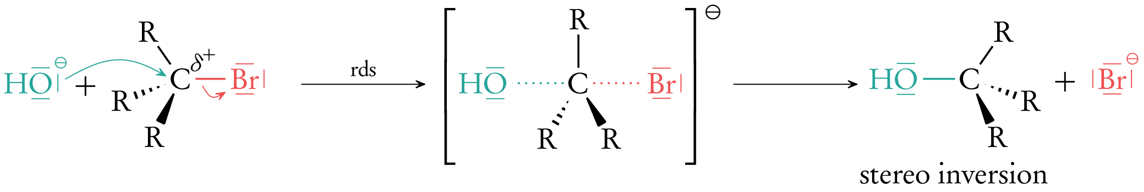


$$R_3C{-}Br + OH^- \longrightarrow R_3C{-}OH + Br^-$$

S_N1 mechanism



S_N2 mechanism

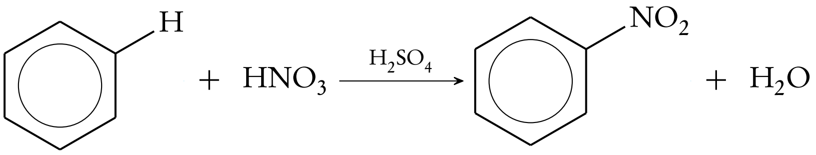


	S_N1 favoured	S_N2 favoured
1° — 3°	3° carbons have greater positive inductive effect: the formation of the carbocation intermediate is easier	1° carbons have less steric hindrance, making the approach of the nucleophile easier
solvent	(carbocat)ions are stabilised through solvation in aqueous solutions and other protic solvents (solvents able to form H-bonds, so containing —OH or —NH).	aprotic solvents not able to form H-bonds. The reactant OH^- is less stabilised, increasing its nucleophilic strength, favouring S_N2.

For nucleophilic substitution reactions on 2° carbons both mechanisms will occur and compete, so only then does the solvent become directing to favour either mechanism.

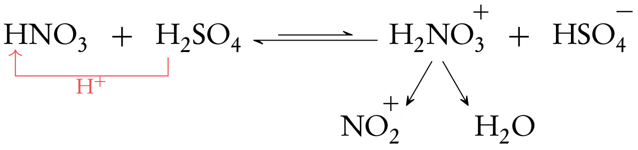
10.4.4 Electrophilic substitution on benzene

Benzene undergoes substitution reactions rather than addition. The typical reaction is of benzene with the very strong electrophile NO_2^+ derived from nitric acid (HNO_3):

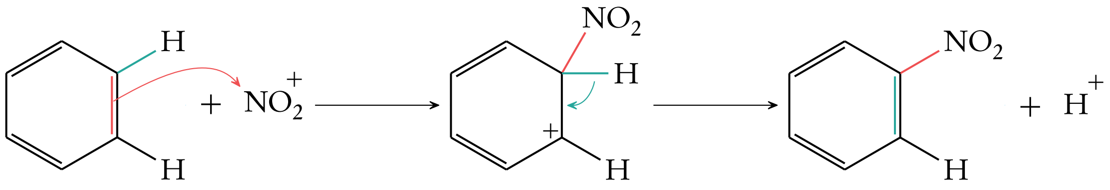


HNO_3 alone is not reactive enough to react with the resonance stabilised benzene molecule. But NO_2^+ is; formed from nitric acid (HNO_3) with sulfuric acid (H_2SO_4):

Interestingly, in this particular reaction the strong acid HNO_3 reacts as a base by accepting H^+ from H_2SO_4.



The formed $H_2NO_3^+$ is highly unstable and dissociates, forming the strongly electrophilic NO_2^+ that is required to react with benzene:



The mechanism is a great example of how catalysts work: while H_2SO_4 participates in the reaction mechanism, the H^+ that forms recombines with HSO_4^- to regenerate H_2SO_4. During this reaction the amount of H_2SO_4 does not change, but it allows the formation of a reactive species (NO_2^+) that lowers the activation energy.

10.4.5 Electrophilic Markovnikov addition

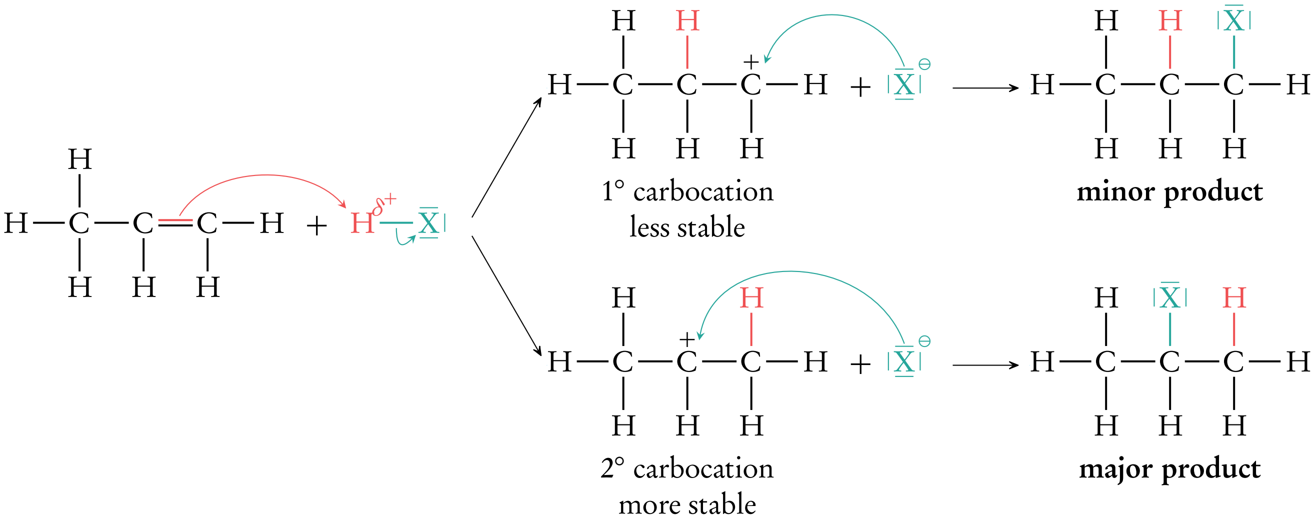
When an asymmetric reactant, such as $\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{X}}$ or $\overset{\delta+}{\mathrm{X}}-\overset{\delta-}{\mathrm{X}}$ (interhalogen), reacts with an asymmetric alkene such as propene $CH_3-CH{=}CH_2$, two structural isomers are formed from two different competing reactions. By understanding the mechanism, we may predict which of the isomers are the major product.

Interhalogens molecules in which only halogens are combined. The simplest is $\mathrm{X}-\mathrm{X}$, where X and X are different, such as:

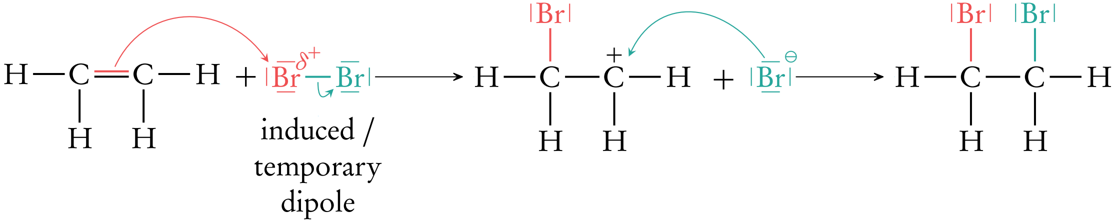
$$\overset{\delta+}{\mathrm{I}}-\overset{\delta-}{\mathrm{Br}} \qquad \overset{\delta+}{\mathrm{Br}}-\overset{\delta-}{\mathrm{Cl}} \qquad \overset{\delta+}{\mathrm{Cl}}-\overset{\delta-}{\mathrm{F}}$$

The addition of $\overset{\delta+}{\mathrm{X}}-\overset{\delta-}{\mathrm{X}}$ occurs via the same mechanism as that of $\overset{\delta+}{\mathrm{H}}-\overset{\delta-}{\mathrm{X}}$.

Markivnikov rule the $-\overset{\delta+}{\mathrm{H}}$ or $-\overset{\delta+}{\mathrm{X}}$ gets attached to the carbon with more hydrogen substituents, and the halide $-\overset{\delta-}{\mathrm{X}}$ attaches to the carbon with more alkyl substituents (more stabilised carbocation).



First the double bond opens to add the electropositive element under formation of the carbocation and halide-ion, then the halide-ion bonds to the carbocation.



10.5 Reactions overview and retrosynthesis

Substitution reactions

	mechanism
$\text{alkane} + X_2 \xrightarrow{\text{UV-light}} \text{halogenoalkane} + HX$	free radical
$\text{halogenoalkane} + X_2 \xrightarrow{\text{UV-light}} \text{dihalogenoalkane} + HX$	free radical
$\text{halogenoalkane} + OH^{\ominus} \longrightarrow \text{alcohol} + X^{\ominus}$	S_N1 and S_N2

Substitution reactions

$$\text{alkene} + H_2 \xrightarrow[\text{heat}]{\text{Ni}} \text{alkane}$$

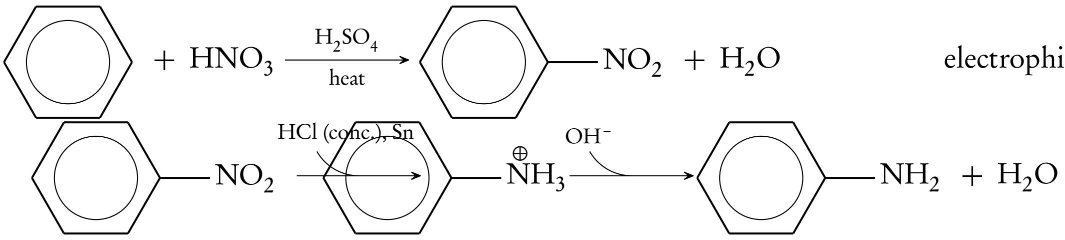
$$\left.\begin{array}{l} \text{alkene} + X_2 \longrightarrow \text{dihalogenoalkane} \\ \text{alkene} + HX \longrightarrow \text{halogenoalkane} \\ \text{alkene} + H_2O \longrightarrow \text{alcohol} \end{array}\right\} \text{electrophillic addition}$$

$$n\ \text{alkene} \longrightarrow (\text{polymer})_n$$

Condensation reactions

$$\text{carboxylic acid} + \text{alcohol} \xrightarrow[\text{heat}]{H_2SO_4} \text{ester} + H_2O$$

Benzene reactions



electrophillic substitution

Alcohol oxidation / carboxylic acid / aldehyde / ketone reduction

$$1^\circ\ \text{alcohol} \xrightleftharpoons[\text{NaBH}_4 \text{ or LiAlH}_4]{H^+/Cr_2O_7^{2-}} \text{aldehyde} + 2H^+ + 2e^- \xrightleftharpoons[\text{LiAlH}_4]{H^+/Cr_2O_7^{2-} + H_2O} \text{carboxylic acid} + 2H^+ + 2e^-$$

$$2^\circ\ \text{alcohol} \xrightleftharpoons[\text{NaBH}_4 \text{ or LiAlH}_4]{H^+/Cr_2O_7^{2-}} \text{ketone} + 2H^+ + 2e^-$$

MEASUREMENT AND DATA PROCESSING

11

Qualitative data refers to all non-numerical information that can be obtained from observations rather than a measurement. Used to identify: which compound?

Quantitative data refers to numerical information obtained from measurements, always associated with systematic and random error/uncertainty. Used to identify: how much compound?

Systematic error refers to flaws in experimental design and machine calibration that lead to an error, which is deviated in a particular direction.

Random Error are statistical fluctuations (in either direction) in the measured data. This can be caused by:

1. Readability or precision limitations of the measuring equipment
2. Uncontrollable changes in the surroundings between trials, such as temperature variations, air currents, . . .

Accuracy refers to how close trials are to a standard/known literature value.
→ High systematic error leads to low accuracy.

Precision refers to how close trials are to each other.
→ High random error leads to low precision.

To decide if an error is systematic or random ask yourself: would repeating the experiment (partially) remove the error?

For example, the boiling point of water at sea level is measured several times. Two different brands of digital temperature probes are used. The temperature readings from brand 1 give have a larger random error than brand 2. To reduce the effects of random error we can increase the number of trials.

	brand 1	brand 2
Trial 1	102.5 °C	96.5 °C
Trial 2	101.5 °C	96.7 °C
Trial 3	97.5 °C	96.6 °C
Average	100.5 °C	96.6 °C

Brand 2 suffers from a large systematic error, but it is very precise. To reduce the systematic error, the temperature probe could be re-calibrated.

11.1 Graphical Techniques

Sketched graphs have labelled but unscaled axes, and are used to show *trends*, such as variables that are (inversely) proportional.

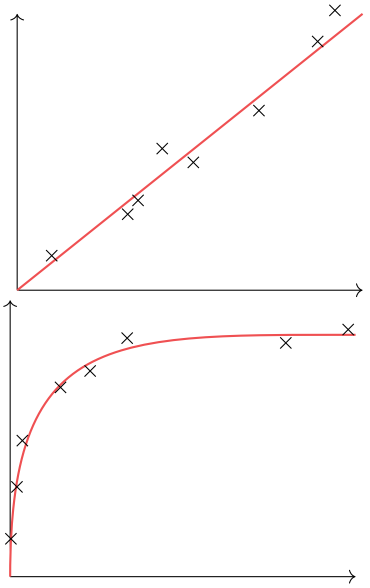
Drawn graphs have labelled and scaled axes, and are used in quantitative measurements.

A graph helps in understanding a trend or mathematical relationship in experimental data. It shows the effect that changing an independent variable (x-axis) has on the dependent variable (y-axis). The value of the dependent variable *depends* on the value of the independent variable.

Line of best fit

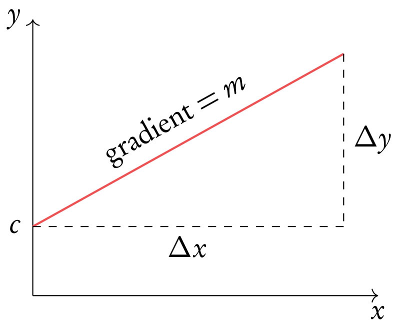
All experimental data is prone to some form of error. A line of best fit shows the appropriate relationship between x and y, taking the variation of individual measurements due to error into account. The line of best fit does not (necessarily) go through all the data points. But it is always a continuous line without sharp "bends" that passes as near to as many points as possible. Lines of best fit can be drawn for any mathematical relationship: linear, quadratic, exponential, etc...

When asked to draw a line of best fit: use a pencil first, and consider if it should pass the origin or not.



Linear graphs

When the dependent variable is proportional to the independent variable, it is called a linear function (i.e. a straight line). The general formula is: $y = mx + c$



The gradient m (slope) of the line expresses the proportionality *factor*:

→ when $m = 2$ then y increases by 2 everytime x increases by 1
→ when $m = 0.43$ then y increases by 0.43 everytime x increases by 1

The value of the gradient can be calculated by: $m = \frac{\Delta y}{\Delta x}$.

When determining the gradient from a given graph, oftentimes *after* drawing the line of best fit, the triangle used to calculate the gradient should be as large as possible. Also use your ruler, and take care to read the values from the graph as precisely as you can!

When $c = 0$, the graph intersects at the origin and y is *directly* proportional to x.

Graphical techniques

The y-intercept: the initial or starting value, when $x = 0$.

The gradient of a curve at a certain point $\left(m = \frac{\Delta y}{\Delta x}\right)$.

Since y/x, the units of the gradient will be the units of y divided by the units of x.

The area under the curve between two points (area $= \Delta y \cdot \Delta x$).

Since $y \cdot x$, the units of the area will be the units of y times the units of x.

Interpolation: a value on a graph between measurements.

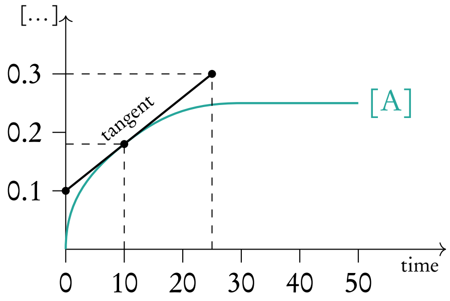
Extrapolation: a value on a graph outside the measurements, assuming that the graph continues the trend.

Example.

When a graph is not linear, the gradient changes continuously. The gradient at a certain point can be determined by first drawing the tangent, and then the gradient m can be determined from a large Δy vs Δx triangle.

Determine the rate of the reaction at $t = 10\,\text{s}$ from the given graph, and derive the units for the rate of reaction.

The rate of reaction is the change in concentration per unit of time, or the gradient in the concentration vs time graph.



Start by drawing the tangent line at $t = 10\,\text{s}$ using a ruler.
Next, find two convenient points on the tangent as far away from each other to calculate the gradient

$$m = \frac{\Delta y}{\Delta x} = \frac{0.30 - 0.10}{25 - 0} = 8.0 \times 10^{-3}$$

To determine the correct units, simply put the units into the formula instead of the values:

$$m = \frac{\Delta y}{\Delta x} = \frac{\text{mol}\,\text{dm}^{-3}}{\text{s}} = \text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}.$$

The rate of the reaction at $t = 10\,\text{s}$ is $8.0 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$.

Inversely proportional

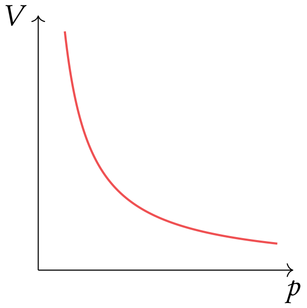
A typical question that involves an inversely proportional relationship is that between the pressure and the volume of a gas, when the mass and temperature are kept constant.

From chapter 1, remember that the ideal gas law can be written as: $nR = \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$

So at constant T: $\frac{p_1 V_1}{\cancel{T_1}} = \frac{p_2 V_2}{\cancel{T_2}} = p_1 V_1 = p_2 V_2$

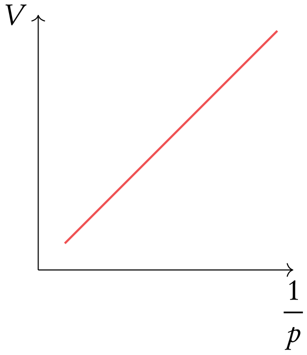
Since $p_1 V_1 = p_2 V_2$, when the pressure is doubled: the volume halves (and vice versa).

This is called inversely proportional, and it produces the graph you see on the right.



Such an inversely proportional function can be displayed as a linear function by changing one variable to its inverse.

For example: change the p-axis to $\frac{1}{p}$.
This technique (as well as manipulation of logs) is also used in chapter 5 on the Arrhenius equation, to get a linear graph between $\ln A$ and $\frac{1}{T}$, with the gradient $m = -\frac{E_a}{R}$.



11.2 Spectroscopic identification

From personal experience of the authors, we can say that it is often difficult to identify the compounds that we create in the lab, as well as their purity. Advanced spectroscopic techniques help us identify the compounds we create.

Spectroscopic methods can give insight in the arrangement of atoms that form a molecule. But often there is no certain definitive answer, and we have to understand that each single technique has strengths and weaknesses.

Oftentimes, chemists combine spectroscopic methods to take advantage of the strengths and weaknesses of each individual method.

List of spectroscopic methods

The operating principles are not required for any of these methods, you will only be tested on knowing how and what information to gather.

Index Hydrogen Deficiency (IHD) also known as the degree of unsaturation, is used to determine the number of H_2 molecules required to convert any molecule to one that is *saturated* and *non-cyclic*.

Mass spectrometry measures the mass of the molecule, and the masses of the fragments that form from the molecule.

Infrared (IR) spectroscopy identify the type of bonds and functional groups present in a molecule.

Proton Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy identifies for hydrogen atoms: 1. their chemical environment, 2. the ratio between the number of hydrogen atoms in the same environment, and 3. the number of neighbouring hydrogen atoms in a molecule.

X-Ray Diffraction identify the lengths and angles of bonds in any type of substance (metal, ionic and molecular).

IHD – index of hydrogen deficiency

The value of IDH = number of rings + number of π bonds

It is equal to the number of H_2 molecules required to convert any molecule to a *saturated* and *non-cyclic* compound. This means that a saturated and non-cyclic compound would have an IHD value of 0.

The index of hydrogen deficiency is given by:

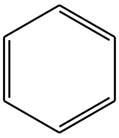
$$\text{IHD} = \frac{2 + 2 \cdot \text{C} + \text{N} - \text{H} - \text{X}}{2}$$

C = number of carbon atoms
H = number of hydrogen atoms
X = number of halogen atoms
N = number of nitrogen atoms

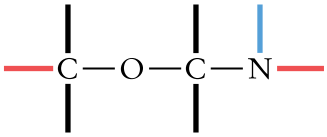
When a structural formula of a molecule is given, the IHD is easily determined, namely by the counting the number of π bonds and rings.

Example.

Benzene has an IHD = 4, because it has 3π bonds and one ring. On the exam, students often forget to add one to the IHD for each ring.



When the molecular formula is given the IHD must be determined by the above given formula. A quick way to remember the formula is by drawing the following structure:



$$-\text{C}-\text{O}-\text{C}-\text{N}-$$

$$\frac{+2 + 2 \cdot \text{C} + \text{N} - \text{H} - \text{X}}{2}$$

- A saturated non-cyclic molecule starts and ends with a hydrogen, so +2.
- Any carbon atom requires 2 hydrogen atoms each, so +2·C.
- Any nitrogen atom requires 2 hydrogen atoms each, so +N.
- The number of oxygen atoms have no influence on the IHD.

Furthermore, since the IHD is about hydrogen *deficiency*, we subtract 1 for every hydrogen we do have. And since halogens replace a hydrogen, we also deduct one for those.

And finally, since the IHD counts the number of H_2 molecules that would be required, we have to divide by 2.