Preparation Course

Chemistry

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1 The Atomic Structure

1.1 The Atom

The **valence shell model** explains that an atom consists of a positively charged **nucleus** located at its center around which negatively charged particles, i.e., **electrons $\mathbf{e^-}$**, are moving along certain orbits, called **electron shells**. The nucleus itself is also home to two types of (composite) particles: positively charged **protons $\mathbf{p^+}$** and neutrally charged **neutrons n**.

While the protons and electrons are attracted to each other electrostatically by the **Coulomb force**—this force attracts (repels) charged particles with opposite (equal) charge—the electrons generally remain in their orbits *at fixed distances from the nucleus* due to the fact that energy comes in **discrete packets called quanta**. In other words, the electrons can only orbit the nucleus at certain discrete energy levels and cannot exist in between two energy states.

Within their respective stable orbits, electrons find themselves in the lowest possible energy state and it *requires* energy for an electron to reside temporarily in another orbit that lies *farther* away from the nucleus. Put differently, electrons in the outer orbits contain more energy than those populating the inner orbits.

That necessary energy to jump to a more distant orbit is procured at the moment when an atom is excited by an incoming discrete packet of light, i.e., a **photon**, that possesses an energy which exactly matches the difference in energy between the two orbits. Put differently, the atom has **absorbed** a photon of light.

Conversely, an electron that momentarily dwells in a higher-energy orbit can fall down to a lower-energy orbit by **sending out** a photon with an energy that corresponds to the energy difference between the two orbits—this only occurs when there is an available slot for the electron in the lower-energy orbit.

What is more, the *closer* to the positively charged nucleus the negatively charged electrons flow, the *more* energy it takes to remove them from their orbits, since the electrostatic force acts more intensely on them. This especially applies to heavier atoms, which house more protons within their nucleus and unleash a larger Coulomb force between the protons and the electrons. This is why it takes higher-energy photons (such as X-rays) to knock out electrons from the innermost regions in heavier atoms.

1.2 Atomic Shells

To move a bit closer to the real-world picture of how electrons act around the atom's nucleus, it is helpful to appreciate that the electron shells contain one or more **subshells**, which in turn consist of one or more electron clouds called **orbitals**. The electron shells are characterized by the **principal quantum number $\boldsymbol{n}$**, whereby the innermost shell is defined by $n = 1$, the next one by $n = 2$, etc. Alternatively, the electron shells have also been assigned a capital letter in alphabetical order, starting from K for the shell closest to the nucleus—the next one is referred to as shell L, the one after that as shell M, etc.

The subshells are associated with the **secondary quantum number $\boldsymbol{l}$**, which determines the *shape* of the electron cloud, i.e., the orbital. The first four orbital types are s, p, d, and f, which correspond to the secondary quantum numbers $l = 0$, $l = 1$, $l = 2$, and $l = 3$, respectively—beyond the orbital type f, the classification follows an alphabetical order. For instance, the subshell s ($l = 0$) of the first electron shell ($n = 1$) is written as 1s, the subshell p ($l = 1$) of the second electron shell ($n = 2$) as 2p, and the subshell d ($l = 2$) of the third electron shell ($n = 3$) as 3d.

There is third quantum number, called the **magnetic quantum number $\boldsymbol{m_l}$**, which indicates the *spatial orientation* of the orbital. Because of the various possibilities in terms of orientation, there can exist multiple orbitals per subshell. The exact number is determined by the expression $2l + 1$. That is, the number of orbitals equals 1 for the s subshell, 3 for the p subshell, 5 for the d subshell, etc.

Due to the nature of electrons, *Pauli's exclusion principle* tells us that there can only be **2 electrons per orbital**—this fact is related to a fourth quantum number, i.e., the spin quantum number s, which is not further discussed here. This means that the number of electrons per subshell is equal to $2 \times (2l + 1)$, or 2 for the s subshell, 6 for the p subshell, 10 for the d subshell, and so on. For instance, an s subshell of the first electron shell fully occupied by electrons is then written as $1s^2$, a p subshell of the second electron shell as $2p^6$, and a d subshell of the third electron shell as $3d^{10}$.

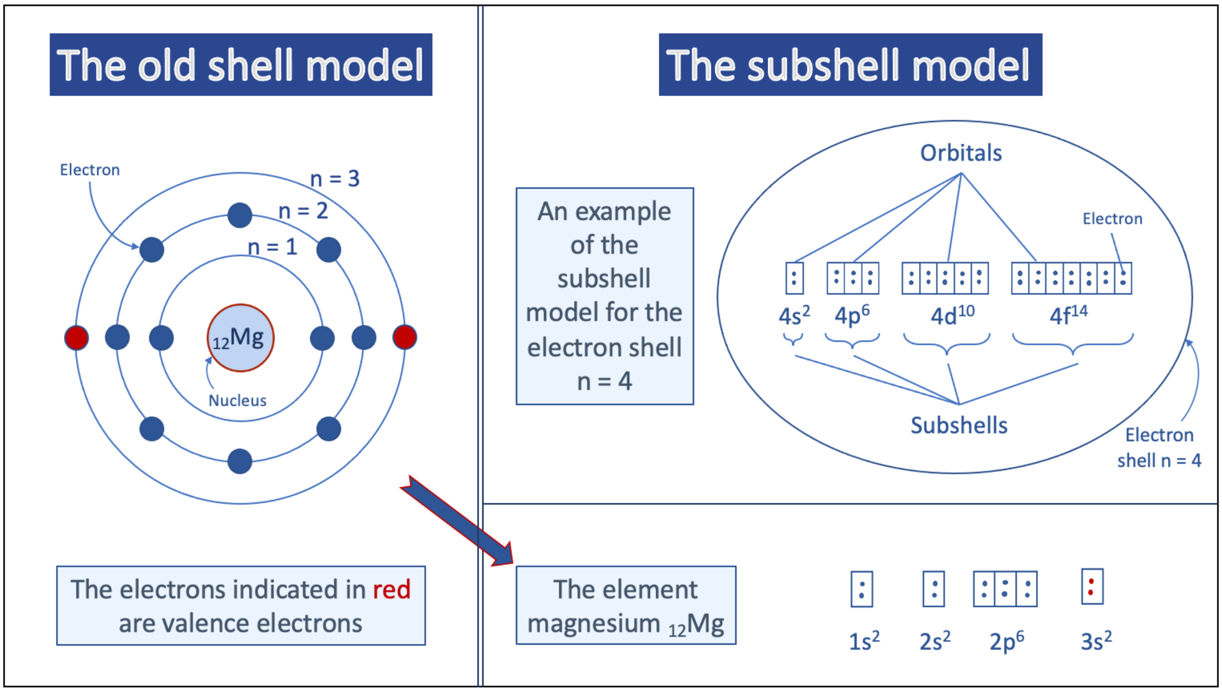


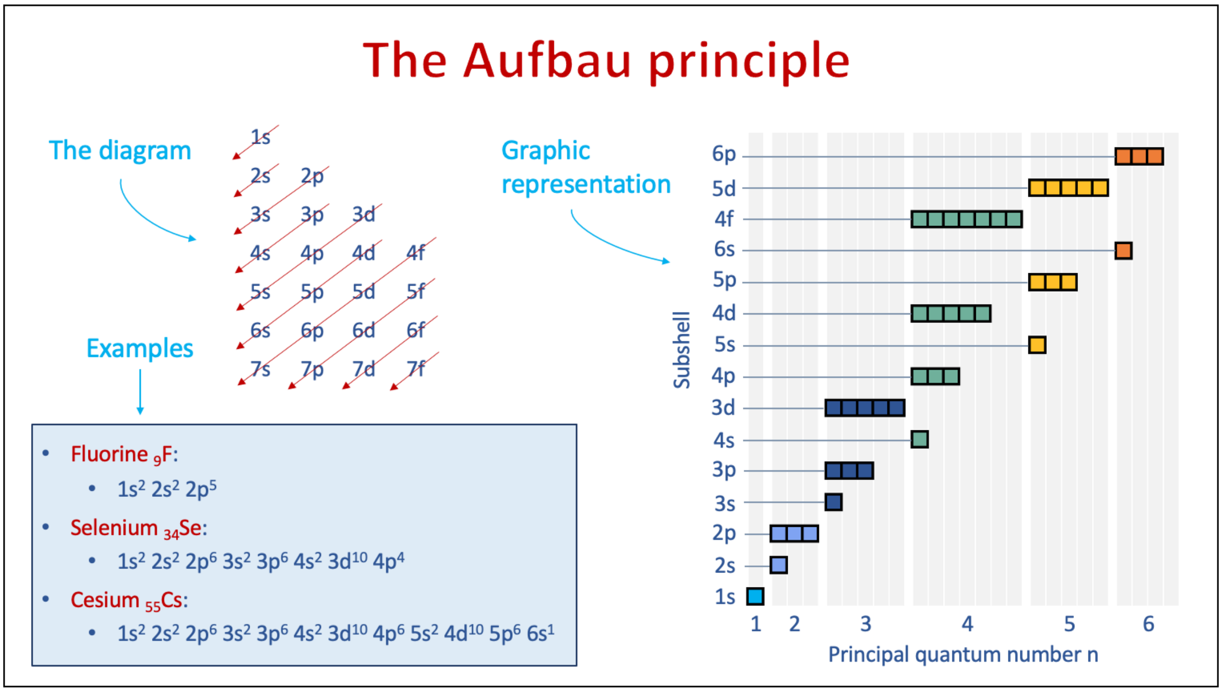
Figure 1.1: The old shell model versus the subshell model of the atom

Finally, the total number of electrons per electron shell is given by the formula $2n^2$. In other words, the first electron shell can accommodate 2 electrons, the second one 8, the third one 18, etc. Together with the knowledge of the maximum number of electrons for each subshell, this sets a limit to the number of subshells per electron shell, i.e., n subshells per electron shell. All the above is summarized by the following equations:

$$\begin{cases} \textit{Number of orbitals per subshell} & = \quad 2l+1 \\ \textit{Number of electrons per subshell} & = \quad 2\times(2l+1) \\ \textit{Number of electrons per electron shell} & = \quad 2n^2 \\ \textit{Number of subshells per electron shell} & = \quad n \end{cases} \tag{1.1}$$

Another tweak to the model described in section 1.1 refers to the fact that electrons within the same *sub*shell, rather than the same electron shell, possess equal energies. Moreover, while it holds in general that the energy of *electron shells* rises as we move farther away from the nucleus (thus with an increasing principal quantum number n), it is more accurate to state that it is the energy within each subsequent *subshell* that is augmenting. This leads to the situation whereby some subshells of *higher* electron shells can have a *lower* energy than those of lower electron shells, and it implies that electrons will first nestle within these lower-energy subshells.

Let us for instance look at the electron configuration for the element calcium. As its nucleus holds 20 protons, the neutrally charged atom has an equal number of electrons orbiting its nucleus. If we would fill the 20 electrons according to increasing principal quantum number n, we obtain an electron configuration of this form: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$. But experiments show that the correct configuration is the following: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. That is, even though $4s^2$ forms part of a higher electron shell, it is energetically preferred to first fill the 4s subshell with electrons, before turning to the 3d subshell of the lower electron shell.



The Aufbau principle

The diagram

Examples

- Fluorine $_9$F:
  - $1s^2\ 2s^2\ 2p^5$
- Selenium $_{34}$Se:
  - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$
- Cesium $_{55}$Cs:
  - $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1$

Graphic representation

Figure 1.2: The Aufbau Principle

In fact, the ascending order in which electrons fill the subshells is dictated by the sum $n+l$, whereby the subshell with the lowest n is given priority in case of equal values of $n+l$; this is known as the **Aufbau principle** or the Madelung rule. This principle tells us that the specific order comes down to this: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6$ etc. Nonetheless, there are chemical elements—20 in total across the three categories of transition metals, lanthanides, and actinides (see section 2)—that deviate from this rule, which is not further examined here. In the case of our example of calcium, we indeed find that $n + l = 4 + 0$ for the 4s subshell is lower than $n + l = 3 + 2$ for the 3d subshell.

An electron configuration is sometimes written in a simplified **coma-separated form (a, b, c, d, ...)**, whereby each slot represents the total number of electrons of the respective electron shell and whereby the totals are mentioned in increasing order of electron shell. For instance, the electron configuration of silicon (with 14 electrons) is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$, which becomes (2, 8, 4) in coma-separated form, as the total for electron shell $n = 1$ is 2, 8 for $n = 2$, and 4 for $n = 3$. Another example is argon (with 18 electrons), whereby the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ is converted into the simplified notation of (2, 8, 8).

When only considering the main-group elements within the Periodic Table—these are the elements that belong to the Groups 1 and 2, and the Groups 13 to 18 of the Periodic Table (see section 2)—then the electrons that belong to the *outermost* electron shell of the atom are the ones that engage in chemical reactions and are referred to as **valence electrons**; hence the name valence shell model. For instance, given the electron configuration of aluminum (with 13 electrons) of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$, the number of valence electrons equals the number of electrons in electron shell $n = 3$, i.e., $2 + 1 = 3$.

1.3 Notation and Atomic Mass

An atom of a particular chemical element within the Periodic Table is distinguished from an atom of another element by *the number of protons* it accommodates within its nucleus. This number is referred to as the **atomic number Z** and is typically written at the bottom left of the symbol of the respective chemical element: $_{\mathrm{Z}}\mathrm{E}$ (with E a particular chemical element)—confusingly, within the Periodic Table the atomic number Z is usually written on top of the element.

What is more, the **mass number A** is defined as the total number of protons and neutrons in the nucleus of an atom, and it closely resembles the actual mass of the atom, called the atomic mass (see further below). The mass number A is usually positioned at the top left of the chemical symbol ($^{\mathrm{A}}\mathrm{E}$). The number of neutrons in an atom can then be found as follows:

$$\begin{cases} \textit{Number of neutrons} & = & \textit{mass number A} & - & \textit{atomic number Z} \\ \#(n) & = & \#(n+p) & - & \#(p) \end{cases} \tag{1.2}$$

When the number of protons equal that of electrons, the atom as a whole is electrically neutral. However, when the atom either loses or gains electrons, it is said to become **ionized**. Positively charged ions (a.k.a. **cations**) have fewer electrons, whereas negatively charged ions (a.k.a. **anions**) have an excess of electrons, with respect to the neutral atom.

The charge of an atom is indicated at the top right of the symbol. For example, the oxygen anion $^{16}_{8}O^{2-}$ has 8 protons, 8 neutrons, and 10 electrons, i.e., 2 more electrons than the neutral element $^{16}_{8}O$. Another example is the sodium cation $^{23}_{11}Na^{+}$, which harbours 11 protons, 12 neutrons, and 10 electrons, i.e., one electron less than its non-ionized counterpart $^{23}_{11}Na$.

The **atomic mass** of a chemical element is usually expressed as the mass *relative to* one twelfth of the mass of the element carbon, which is designated the atomic mass unit (*amu*). In other words, 1 *amu* is measured as $\frac{1}{12}$ of the mass of the atom $^{12}_{6}C$, whereby 1 $amu = 1.66054 \times 10^{-27}$ kg. For example, the atomic mass of the element cesium ($^{133}_{55}C$) is equal to 132.91 amu or $132.91 \times (1.66054 \times 10^{-27}$ kg$) = 2.20702 \times 10^{-25}$ kg.

When writing the mass of protons ($m_p = 1.67262 \times 10^{-27}$ kg), neutrons ($m_n = 1.67492 \times 10^{-27}$ kg), and electrons ($m_e = 9.10939 \times 10^{-31}$ kg) in terms of *amu*, we obtain $m_p = 1.00727$ amu, $m_n = 1.00866$ amu, and $m_e = 5.48580 \times 10^{-4}$ amu, respectively. Considering these relative masses, it becomes apparent that the mass of atoms is predominately determined by the nucleus, i.e., the ensemble of protons and neutrons. This explains why the value of the mass number A of a given element is close to that of the element's atomic mass.

1.4 Isotopes and the Relative Atomic Mass

The number of neutrons within the nucleus of atoms of the *same* chemical element can vary. That is, one atom can take on several *stable* forms with each time a different number of neutrons. These various forms are designated as **isotopes**, whereby the mass number A changes for every isotope of the element while the atomic number Z remains the same. One *specific* isotope is then called a **nuclide**, which is indicated by the **symbol** $\mathbf{^{A}_{Z}E}$. In other words, to qualify as a nuclide, *both* the atomic number Z and the mass number A must be known.

For instance, one of the isotopes of the element krypton ($^{84}_{36}Kr$) is the nuclide $^{80}_{36}Kr$, which contains $80 - 36 = 44$ neutrons instead of the usual $84 - 36 = 48$ for the standard krypton atom. As a counterexample, an isotope with mass number 50 is not a nuclide, given that it is not specified or unique, because it can refer both to the isotope 50 of titanium ($^{50}_{22}Ti$) and to the isotope 50 of vanadium ($^{50}_{23}V$)—these two particular isotopes are indeed nuclides, as their respective atomic number is now identified.

The **relative atomic mass $\mathbf{A_r}$** of a chemical element is defined as the *weighted* average of the atomic masses of all the stable isotopes of that element per *amu*, and it is this value that is indicated below the symbol of the chemical elements within the Periodic Table. As stated previously, the atomic mass is usually approximated by the mass number A. The weights applied are the relative abundances of the isotopes, i.e., the relative extent to which the different isotopes are naturally present on Earth (given in percentages). Given that the atomic masses of the elements are expressed in *amu*, the relative atomic mass A_r is unitless and is formulated as:

$$\textit{Relative atomic mass } A_r = \sum_{i=1}^{n} \left(\frac{\textit{natural abundance (\%)}}{100} \right)_i \times \textit{(mass number A)}_i \quad (1.3)$$

whereby i runs from 1 to n, with n the total number of isotopes. For example, the element palladium has six stable isotopes, i.e., $^{102}_{46}$Pd, $^{104}_{46}$Pd, $^{105}_{46}$Pd, $^{106}_{46}$Pd, $^{108}_{46}$Pd, and $^{110}_{46}$Pd, with natural abundances of 1.02%, 11.14%, 22.33%, 27.33%, 26.46%, and 11.72%, respectively. Its relative atomic mass is then calculated as $(0.0102 \times 102) + (0.1114 \times 104) + (0.2233 \times 105) + (0.2733 \times 106) + (0.2646 \times 108) + (0.1172 \times 110) = 106.51$. Another example involves the relative atomic mass of 6.92 for the chemical element lithium. If the relative abundance of the first of the two stable isotopes $^{6}_{3}$Li and $^{7}_{3}$Li is equal to 7.59%, then the natural abundance of the second isotope is calculated as $(\frac{6.92 - 0.0759 \times 6}{7}) \times 100 = 92.35\%$.

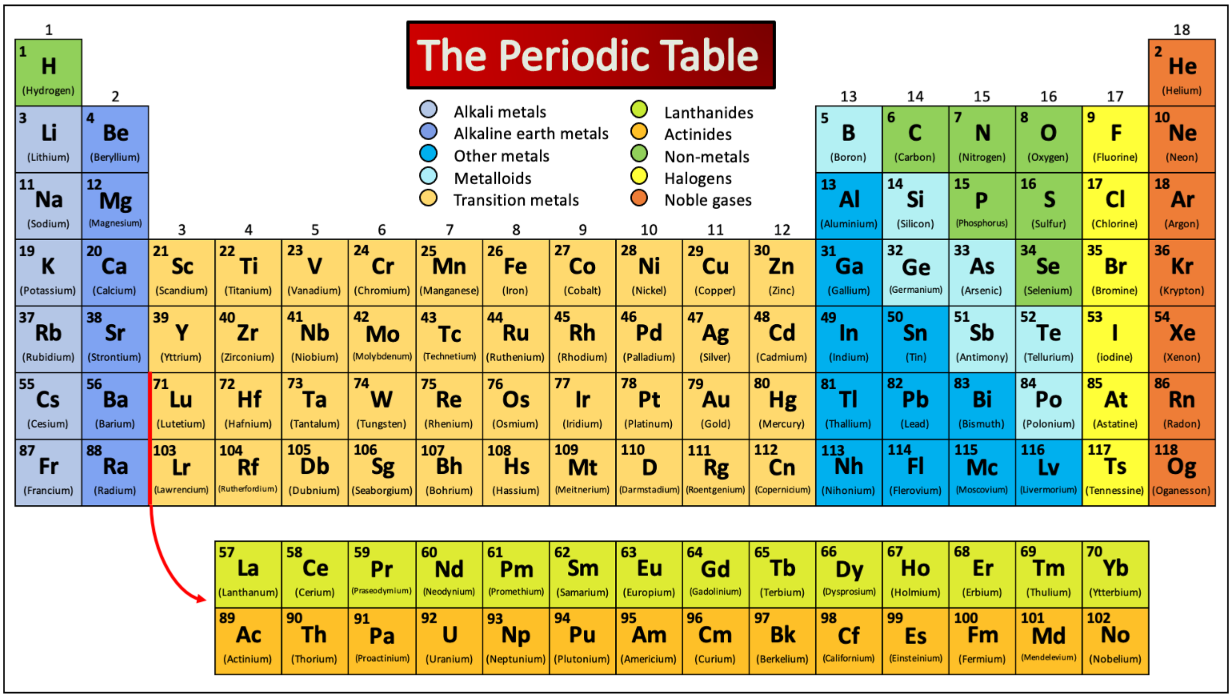
2 The Periodic Table

2.1 The Main Features

The **Periodic Table** is a systematic and visual representation of all the different **118 natural and synthetic chemical elements** that have been known to exist up until today. The final 24 elements in the table, i.e., the elements beyond and including the element americium $_{95}$Am, are **synthetic**, meaning that they do not occur naturally on Earth but have been artificially created by means of human intervention. Also, the final 35 elements, i.e., the elements beyond and including the element polonium $_{84}$Po, are **radioactive**, which implies that their nucleus is unstable and will undergo certain nuclear transformations.

The rows in the Periodic Table are referred to as **Periods**, while the columns are called **Groups**. There are 7 Periods and 18 Groups, whereby the number of the Period *increases* as one goes *down* a Group and whereby the Group number *goes up* as one moves from *left to right* across a certain Period.

In addition, all the chemical elements within the Periodic Table have been assigned their specific spot according to their atomic number Z. More precisely, the **elements are arranged in the order of increasing Z**. That is, the element with the lowest number ($_1$H) sits at the top left of the Periodic Table, whereas the element with the highest Z ($_{118}$Og) is positioned at the bottom right.



The Periodic Table

● Alkali metals
● Alkaline earth metals
● Other metals
● Metalloids
● Transition metals
● Lanthanides
● Actinides
● Non-metals
● Halogens
● Noble gases

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H (Hydrogen)																	2 He (Helium)
3 Li (Lithium)	4 Be (Beryllium)											5 B (Boron)	6 C (Carbon)	7 N (Nitrogen)	8 O (Oxygen)	9 F (Fluorine)	10 Ne (Neon)
11 Na (Sodium)	12 Mg (Magnesium)											13 Al (Aluminium)	14 Si (Silicon)	15 P (Phosphorus)	16 S (Sulfur)	17 Cl (Chlorine)	18 Ar (Argon)
19 K (Potassium)	20 Ca (Calcium)	21 Sc (Scandium)	22 Ti (Titanium)	23 V (Vanadium)	24 Cr (Chromium)	25 Mn (Manganese)	26 Fe (Iron)	27 Co (Cobalt)	28 Ni (Nickel)	29 Cu (Copper)	30 Zn (Zinc)	31 Ga (Gallium)	32 Ge (Germanium)	33 As (Arsenic)	34 Se (Selenium)	35 Br (Bromine)	36 Kr (Krypton)
37 Rb (Rubidium)	38 Sr (Strontium)	39 Y (Yttrium)	40 Zr (Zirconium)	41 Nb (Niobium)	42 Mo (Molybdenum)	43 Tc (Technetium)	44 Ru (Ruthenium)	45 Rh (Rhodium)	46 Pd (Palladium)	47 Ag (Silver)	48 Cd (Cadmium)	49 In (Indium)	50 Sn (Tin)	51 Sb (Antimony)	52 Te (Tellurium)	53 I (iodine)	54 Xe (Xenon)
55 Cs (Cesium)	56 Ba (Barium)	71 Lu (Lutetium)	72 Hf (Hafnium)	73 Ta (Tantalum)	74 W (Tungsten)	75 Re (Rhenium)	76 Os (Osmium)	77 Ir (Iridium)	78 Pt (Platinum)	79 Au (Gold)	80 Hg (Mercury)	81 Tl (Thallium)	82 Pb (Lead)	83 Bi (Bismuth)	84 Po (Polonium)	85 At (Astatine)	86 Rn (Radon)
87 Fr (Francium)	88 Ra (Radium)	103 Lr (Lawrencium)	104 Rf (Rutherfordium)	105 Db (Dubnium)	106 Sg (Seaborgium)	107 Bh (Bohrium)	108 Hs (Hassium)	109 Mt (Meitnerium)	110 D (Darmstadium)	111 Rg (Roentgenium)	112 Cn (Copernicium)	113 Nh (Nihonium)	114 Fl (Flerovium)	115 Mc (Moscovium)	116 Lv (Livermorium)	117 Ts (Tennessine)	118 Og (Oganesson)
			57 La (Lanthanum)	58 Ce (Cerium)	59 Pr (Praseodymium)	60 Nd (Neodynium)	61 Pm (Promethium)	62 Sm (Samarium)	63 Eu (Europium)	64 Gd (Gadolinium)	65 Tb (Terbium)	66 Dy (Dysprosium)	67 Ho (Holmium)	68 Er (Erbium)	69 Tm (Thulium)	70 Yb (Ytterbium)	
			89 Ac (Actinium)	90 Th (Thorium)	91 Pa (Proactinium)	92 U (Uranium)	93 Np (Neptunium)	94 Pu (Plutonium)	95 Am (Americium)	96 Cm (Curium)	97 Bk (Berkelium)	98 Cf (Californium)	99 Es (Einsteinium)	100 Fm (Fermium)	101 Md (Mendelevium)	102 No (Nobelium)	

Figure 2.1: The Periodic Table

Based on a range of similar physical and chemical properties, various **element families** have been identified within the Periodic Table: alkali metals (Group 1 minus the element hydrogen $_1$H), alkaline earth metals (Group 2), the transition metals (Groups 3 to 12; this family contains two subfamilies: the lanthanides and the actinides), halogens (Group 17), and noble gases (Group 18). Other element families that do not belong to a specific Group are referred to as other metals, metalloids, and non-metals (see Fig. 2.1). Remark that the halogens and noble gases also qualify as ”*not being metal*”, so that it becomes apparent that the non-metallic elements aggregate at the right-hand side of the Periodic Table.

The **main-group elements** are defined as the elements that are not transition metals. Put differently, the main-group elements are all the elements that belong to the Groups 1 and 2, and the Groups 13 to 18.

2.2 Connection to the Subshell Model

Central to the understanding of the various structural relationships between the physical and chemical properties of the different elements—this is discussed in greater detail in sections 2.3, 6, 7, and 14—is their **position** within the Periodic Table. That is to say, there exists a connection between the electron configuration of the elements as discussed in the context of the subshell model (see section 1.2) and their specifically assigned position within the Periodic Table.

When it comes to the Periods, the **Period number** corresponds to the *highest principal quantum number n* present in the electron configuration of all the elements of that particular period. What is more, for every period that highest principal quantum number n is associated with either the s orbital or both the s and p orbital. For example, the electron configuration of the element nitrogen ($_7$N), which belongs to period 2, is $1s^2\ \underline{2s}^2\ \underline{2p}^3$, that of the element potassium ($_{19}$K) in period 4 is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \underline{4s}^1$, and that of the element tin ($_{50}$Sn) in period 5 is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ \underline{5s}^2\ 4d^{10}\ \underline{5p}^2$.

Since the elements are ordered by their atomic number Z, it follows that the number of electrons also rise with increasing Period number. From that perspective, the electron configuration of higher-Z elements builds in a certain sense on those of the lower-Z elements. For that reason, higher-Z elements that belong to Period n (with $n \geq 2$) are usually expressed in terms of the electron configuration of the noble gas of Period $n - 1$. For example, instead of writing $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ for the electron configuration of the element phosphorus $_{15}$P (which belongs to Period 3), it can be written more succinctly as $[Ne]\ 3s^2\ 3p^3$, whereby $[Ne]$ is equal to $1s^2\ 2s^2\ 2p^6$ and refers to the noble gas neon of Period 2. Another example is germanium $_{32}$Ge, whose shorthand electron configuration is formulated as $[Ar]\ 4s^2\ 3d^{10}\ 4p^2$.

Regarding the *main-group elements*, the total sum of electrons within the s and p orbitals of the outermost electron shell n—which corresponds to the Period n—equals the number of valence electrons and additionally indicates the **Group number** of the respective element (for the Groups 13 to 18, one has to consider only the second digit of the Group number to find the number of valence electrons). For instance, the element beryllium $_4$Be of Group $\underline{2}$ has $\underline{2}$ valence electrons, which sit in the subshell $2s^2$, and the element sulphur $_{16}$S of Group $1\underline{6}$ has $\underline{6}$ valence electrons, which is the total of electrons within the subshells $3s^2$ and $3p^4$. One exception is the noble gas helium $_2$He of Group 18, which has 2 valence electrons.

As a matter of fact, there is a systematic connection between the different Groups and the electron configuration of the elements. With regard to Group 1 and Group 2, the outer electron shell of *all* the elements in one particular Group has the same form, i.e., ns^1 and ns^2, respectively (with n the Period number). This is why Group 1 and Group 2 combined, together with the element helium, is called the **s-block**. With respect to the Groups 13 to 18, the outer electron shell of all the elements in Group 13 takes on the form $ns^2\ np^1$, for the Group 14 this becomes $ns^2\ np^2$, and so on until Group 18, whose outer electron shell has the form of $ns^2\ np^6$. As it is the p subshell that is being filled for these 6 Groups, they are collectively referred to as the **p-block**. For similar reasons, the lanthanides and actinides together are called the **f-block** (with a few exceptions), while the ensemble of the remaining transition metals (Groups 3 to 12) is known as the **d-block**.

2.3 Trends in Reactivity

To drive home the point of the previous section, all the elements within one single Group—considering only the main-group elements—have the *same* number of valence electrons, which in turn explains why elements of the same Group exhibit *similar chemical properties*, as it is the valence electrons that engage in chemical reactions (see also sections 3 and 7). For instance, the noble gases (Group 18) chemically distinguish themselves from the other Groups by the fact that they typically react very little with other elements—their specific electronic configuration (the so-called electron octet structure) is very stable—which is why they are often called inert gases and exist as monoatomic gases.

Moreover, both alkali metals (Group 1) and halogens (Group 17) are among the **most reactive elements** in the Periodic Table, but act in the opposite direction. That is to say, alkali metals rather eagerly wish to get rid of an electron and become cations with a charge of plus 1, e.g., Na^+, whereas halogens have a strong urge to capture an additional electron, converting themselves into anions with a charge of minus 1, e.g., F^-. The underlying reason for the behaviour of these Groups is their tendency to strive for the stable octet structure of the noble gases—this is known as the **octet rule**. A similar, but less reactive behaviour is manifested by the Group 2 (the alkaline earth metals) and Group 16 elements (often referred to as chalcogens): generally, the alkaline earth metals react to turn into plus 2-cations, e.g., Mg^{2+}, whereas Group 16 elements develop into minus 2-anions, e.g., O^{2-}.

On top of that, there is also a **periodic trend** within the Groups of metals in terms of reactivity. That is, moving down **Group 1 and Group 2**, i.e., the Period number n increases, the negatively charged valence electrons sit each time farther away from the positively charged nucleus—the atom grows in size—and thus experience less electrostatic force. This translates into a greater ease with which the atoms can shed their valence electrons, which implies a *more pronounced* reactive behaviour of the atoms *towards the bottom* of both Groups—the required energy for an atom to get rid of an electron is called the **ionization energy (IE)**, which generally follows a *declining* trend *down* a Group.

Moving to the right-hand side of the Periodic Table to **Group 17**, an opposite periodic trend in terms of reactivity arises for the halogens. With an increasing Period number n down the Group, the extra valence electron that the halogens wish to capture experiences an ever weakening attractive force by the nucleus, as the distance to the nucleus grows larger. In other words, the atoms becomes less eager to accept an additional electron. As a result, the extent of reactivity among Group 17 elements *diminishes* as one moves *down* the Group—the change in energy of the atom or ion when an extra electron is added is designated the **electron affinity (EA)**, which is generally *more negative towards the top* of a Group (lower Period number n), meaning that, rather than requiring energy, energy is being released.

3 Chemical Reactions

3.1 A definition

A **chemical reaction** can be described as the process whereby the atoms and electrons of various molecules are being rearranged and interchanged. The molecules that go into the chemical reaction are known as **reactants**, whereas the chemical substances that come out of the reaction are called **products**. Keep in mind that the nuclei of the atoms are *not altered* during chemical reactions; that is, no nuclear transformations take place, so that the mass number A and the atomic number Z of the elements do not change.

A **molecule** is defined as an aggregation of two or more atoms that are held together through chemical bonds. A **compound** is a molecule whereby at least two atoms belong to *different* chemical elements. As a result, all compounds are molecules, yet not all molecules are compounds. For instance, ozone with its chemical formula O_3 is a molecule but not a compound, as there is only one type of element present in the molecule.

3.2 Ionic and Covalent Compounds

Various types of chemical bonds exist between atoms, including ionic and covalent bonding. **Ionic bonds** are typically forged *between ion metals and non-metals* whereby one or more valence electrons are *exchanged*, whereas **covalent bonds** occur *between non-metals* (or between non-metals and metalloids) that *share* some of their valence electrons—these two classes of bonds are further discussed in section 6.

Examples of the most common non-metal compound ions are carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), nitrate (NH_3^{-}), phosphate (PO_4^{3-}), and hydroxide (OH^{-}), which form for instance the following **ionic compounds**: calcium carbonate ($CaCO_3$), potassium sulfate (K_2SO_4), ammonium nitrate (NH_4NO_3), aluminum phosphate ($AlPO_4$), and sodium hydroxide ($NaOH$). Other common examples of ionic compounds are sodium chloride or table salt ($NaCl$), potassium chloride (KCl), magnesium fluoride (MgF_2), and lithium fluoride (LiF).

Some of the more common **covalent compounds** include water (H_2O), methane (CH_4), ammonia (NH_3), carbon chloride (CCl_4), nitrogen dioxide (NO_2), fluorine gas (F_2), carbon dioxide (CO_2), silicon dioxide (SiO_2), and hydrogen peroxide (H_2O_2).

3.3 Chemical Equations

During a chemical reaction, the various compounds and molecules may alter their chemical and physical properties, including their state of matter. Physical objects, including chemical molecules, can broadly speaking take on three states of matter: solid (s), liquid (l), and gas (g)—see section 15 for more details. However, in chemistry there is a fourth state of matter called aqueous solution (aq), which indicates that a compound is dissolved in water.

A **chemical equation** expresses mathematically what the initial and final state of a chemical reaction is. Moreover, given that no nuclei can be destroyed or created in a chemical reaction, the total number of atoms of each element must remain unchanged before and after the reaction. This means that a chemical equation must be **balanced**—put another way, a chemical equation has to comply with the law of conservation of mass. For instance, the following chemical equation shows what happens when the alkali metal potassium (K) is put into contact with water (H_2O):

$$\ldots \underset{\text{solid}}{K(s)} + \ldots \underset{\text{liquid}}{H_2O(l)} \longrightarrow \ldots \underset{\text{aqueous}}{KOH(aq)} + \ldots \underset{\text{gas}}{H_2(g)} \tag{3.1}$$

However, Equation 3.1 is not yet balanced, as there are 2 atoms of hydrogen in the reactant water and a total of 3 hydrogen atoms amongst the two reaction products, which clearly violates the fact that no nuclei can be created in a chemical reaction. To balance out the chemical equation, we need to write numerical coefficients in front of the various compounds and molecules—these coefficients are called **stoichiometric coefficients**—whereby we select the smallest possible *integer* values. Equation 3.2 provides the final, balanced chemical equation, which says that for every 2 atoms of potassium (K) reacting with 2 compounds of water (H_2O), the chemical reaction returns 2 potassium hydroxide (KOH) compounds and one hydrogen gas (H_2) molecule:

$$\underset{\text{solid}}{2\,K(s)} + \underset{\text{liquid}}{2\,H_2O(l)} \longrightarrow \underset{\text{aqueous}}{2\,KOH(aq)} + \underset{\text{gas}}{H_2(g)} \tag{3.2}$$

Ionic equations are chemical equations whereby the ionic compounds, when dissolved in aqueous solution, are expressed as dissociated ions. That is to say, when ionic compounds disintegrate in, let's say, water, the different ions are physically separated from one another, whereas with covalent compounds dissolved in water, the individual molecules move away from each other and remain intact. For example, the below two ionic equations illustrate how carbon chloride ($CaCl_2$) and table salt (NaCl) are dissociated in water:

$$\begin{cases} CaCl_2(s) & \xrightarrow{H_2O} & Ca^{2+}(aq) + 2\,Cl^{-}(aq) \\ NaCl(s) & \xrightarrow{H_2O} & Na^{+}(aq) + Cl^{-}(aq) \end{cases} \tag{3.3}$$

When different ionic compounds are dissolved, not all of the dissociated ions react with one another. The ions that do not undergo any chemical change are referred to as **spectator ions**. This means that the spectator ions appear both at the reactant and product side of the ionic equation. Canceling them at both sides gives what is called the **net ionic equation**.

The below example shows the different steps to arrive at the net ionic equation in the case that magnesium sulfate ($MgSO_4$) and barium nitrate ($Ba(NO_3)_2$) react in aqueous solution to produce magnesium nitrate ($Mg(NO_3)_2$) and barium sulfate ($BaSO_4$):

- Step 1: Write the balanced chemical reaction
  $$\mathrm{MgSO_4}(aq) + \mathrm{Ba(NO_3)_2}(aq) \longrightarrow \mathrm{Mg(NO_3)_2}(aq) + \mathrm{BaSO_4}(s)$$
- Step 2: Convert the chemical reaction into an ionic equation
  $$\mathrm{Mg^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq) + \mathrm{Ba^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq) + \mathrm{BaSO_4}(s)$$
  (3.4)
- Step 3: Identify the spectator ions
  $$\cancel{\mathrm{Mg^{2+}}(aq)} + \mathrm{SO_4^{2-}}(aq) + \mathrm{Ba^{2+}}(aq) + \cancel{2\,\mathrm{NO_3^-}(aq)} \longrightarrow \cancel{\mathrm{Mg^{2+}}(aq)} + \cancel{2\,\mathrm{NO_3^-}(aq)} + \mathrm{BaSO_4}(s)$$
- Step 4: Write the net ionic equation
  $$\mathrm{SO_4^{2-}}(aq) + \mathrm{Ba^{2+}}(aq) \longrightarrow \mathrm{BaSO_4}(s)$$

The above example is an illustration of a **displacement reaction**—more accurately, this particular example represents a double displacement reaction—which is one of two types of ionic equations, with the **neutralization reaction** being the other one. In a *double displacement reaction*, the two ion metals swap places in the respective reactant compounds due to the fact that one metal is more reactive than the other—in the above example, barium (Ba) is the more reactive metal (see section 14.1)—to form two new compounds, whereby one is an insoluble solid called a *precipitate*—in our example, this is the barium sulfate ($\mathrm{BaSO_4}$) compound.

In a *neutralization reaction*, an acid and a base react together to generate the formation of a salt and water as products, so that the acidity (expressed in pH value) becomes more neutralized—see section 9 for a definition of acids, bases, salts, and pH. For instance, nitric acid ($\mathrm{HNO_3}$) reacts with the base strontium hydroxide ($\mathrm{Sr(OH)_2}$), which is an ionic compound, to produce water ($\mathrm{H_2O}$) and the soluble salt strontium nitrate ($\mathrm{Sr(NO_3)_2}$):

- Step 1: Write the balanced chemical reaction
  $$\underset{\text{acid}}{2\,\mathrm{HNO_3}(aq)} + \underset{\text{base}}{\mathrm{Sr(OH)_2}(aq)} \longrightarrow \underset{\text{water}}{2\,\mathrm{H_2O}(l)} + \underset{\text{salt}}{\mathrm{Sr(NO_3)_2}(aq)}$$
- Step 2: Convert the chemical reaction into an ionic equation
  $$2\,\mathrm{H^+}(aq) + 2\,\mathrm{NO_3^-}(aq) + \mathrm{Sr^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow 2\,\mathrm{H_2O}(l) + \mathrm{Sr^{2+}}(aq) + 2\,\mathrm{NO_3^-}(aq)$$
  (3.5)
- Step 3: Identify the spectator ions
  $$2\,\mathrm{H^+}(aq) + \cancel{2\,\mathrm{NO_3^-}(aq)} + \cancel{\mathrm{Sr^{2+}}(aq)} + 2\,\mathrm{OH^-}(aq) \longrightarrow 2\,\mathrm{H_2O}(l) + \cancel{\mathrm{Sr^{2+}}(aq)} + \cancel{2\,\mathrm{NO_3^-}(aq)}$$
- Step 4: Write the net ionic equation
  $$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(l)$$

In the final step of Example 3.5, the stoichiometric coefficients 2 have been replaced by 1, since we need to write the *smallest* possible integer values in a balanced chemical reaction. What is more, all neutralization reactions end up with that same net ionic equation (under the condition that we consider equations that only contain both strong acids and strong bases, which dissolve completely; see section 9 for more details). To verify that claim, let us consider another example whereby sulphuric acid (H_2SO_4) reacts with the base sodium hydroxide (NaOH) to return water as well as the soluble salt sodium sulfate (Na_2SO_4):

- Step 1: Write the balanced chemical reaction

  $H_2SO_4(aq) + 2\,NaOH(aq) \longrightarrow 2\,H_2O(l) + Na_2SO_4(aq)$

- Step 2: Convert the chemical reaction into an ionic equation

  $2\,H^+(aq) + SO_4^{2-}(aq) + 2\,Na^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l) + 2\,Na^+(aq) + SO_4^{2-}(aq)$

- Step 3: Identify the spectator ions

  $2\,H^+(aq) + \cancel{SO_4^{2-}(aq)} + \cancel{2\,Na^+(aq)} + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l) + \cancel{2\,Na^+(aq)} + \cancel{SO_4^{2-}(aq)}$

- Step 4: Write the net ionic equation

  $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

(3.6)

Ionic half-equations or half-reactions are chemical equations whereby atoms or molecules either lose electrons (called **oxidation**) or gain electrons (called **reduction**), and the combination of two half-equations gives a net ionic equation. Half-equations form the basis of redox reactions and electrolysis, which will be discussed in more detail in section 5 and 12, respectively. Apart from the requirement in chemical equations to uphold the conservation of mass, it is important to keep in mind in the context of half-equations that *also electric charges must be preserved.* As a rule of thumb, in order to construct a half-equation, it is useful to first balance the number of atoms of each element and in a next step the charges. For example, to write the half-equation for converting the bromide ion (Br^-) into the bromide molecule (Br_2)—this reaction represents oxidation—the following steps are taken:

- Step 1: Write the crude half-reaction

  $Br^-(aq) \longrightarrow Br_2(l)$

- Step 2: Balance the number of atoms

  $2\,Br^-(aq) \longrightarrow Br_2(l)$

- Step 3: Balancing the electric charges gives the half-equation

  $2\,Br^-(aq) \longrightarrow Br_2(l) + 2\,e^-$

(3.7)

Let us look at another example whereby we extract two half-equations from a chemical reaction. Suppose that in a displacement reaction magnesium (Mg) kicks out lead from a solution of lead(II) nitrate ($Pb(NO_3)_2$), thereby producing magnesium nitrate ($Mg(NO_3)_2$) and lead (Pb). The half-equations are constructed as follows:

- Step 1: Write the balanced chemical reaction
  $\mathrm{Mg}(s) + \mathrm{Pb(NO_3)_2}(aq) \longrightarrow \mathrm{Mg(NO_3)_2}(aq) + \mathrm{Pb}(s)$
- Step 2: Write the net ionic equation
  $\mathrm{Mg}(s) + \mathrm{Pb^{2+}}(aq) \longrightarrow \mathrm{Mg^{2+}}(aq) + \mathrm{Pb}(s)$

(3.8)

- Step 3: Write the half-equation for magnesium (oxidation)
  $\mathrm{Mg}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) \quad \Rightarrow \quad \mathrm{Mg}(s) \longrightarrow \mathrm{Mg^{2+}}(aq) + 2\,\mathrm{e^-}$
- Step 4: Write the half-equation for lead (reduction)
  $\mathrm{Pb^{2+}}(aq) \longrightarrow \mathrm{Pb}(s) \quad \Rightarrow \quad \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Pb}(s)$

In the next example, we reverse the question, whereby we start from 2 crude half-equations and wish to combine them into a single net ionic equation. What is crucial during the step of combination is that the total number of electrons is balanced. What we are given is the following information: chlorine gas oxidizes iron(II) ions to iron(III) ions, whereby chlorine is reduced to chloride ions. These steps lead us to the ionic net equation:

- Step 1: Write the crude half-reaction for chlorine
  $\mathrm{Cl_2}(g) \longrightarrow \mathrm{Cl^-}(aq)$
- Step 2: Balance the half-reaction (reduction)
  $\mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-}(aq)$
- Step 3: Write the crude half-reaction for iron
  $\mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq)$
- Step 4: Balance the half-reaction (oxidation)
  $\mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}$

(3.9)

- Step 5: Balance the electrons
  $[\ \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-}(aq)\ ]\times 1$
  $[\ \mathrm{Fe^{2+}}(aq) \longrightarrow \mathrm{Fe^{3+}}(aq) + \mathrm{e^-}\ ]\times 2$
- Step 6: Add the two half-reactions together
  $\mathrm{Cl_2}(g) + \cancel{2\,\mathrm{e^-}} + 2\,\mathrm{Fe^{2+}}(aq) \longrightarrow 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Fe^{3+}}(aq) + \cancel{2\,\mathrm{e^-}}$
  $\mathrm{Cl_2}(g) + 2\,\mathrm{Fe^{2+}}(aq) \longrightarrow 2\,\mathrm{Cl^-}(aq) + 2\,\mathrm{Fe^{3+}}(aq)$

For more complicated ionic compounds, the operation of balancing the half-reaction may include adding hydrogen ions (H^+), water molecules (H_2O), or hydroxide ions (OH^-). In the case of **acidic conditions**, the previously mentioned rule of thumb (see the paragraph above Example 3.7) is expanded in the following way: first, balance the major elements except oxygen and hydrogen; second, balance the oxygen atoms by introducing water molecules (H_2O); third, balance the hydrogen atoms by adding hydrogen ions (H^+); and, finally, balance the charges.

In the context of **basic conditions**, we need to get rid of the hydrogen ions by relying on the *autoionization formula of water*, i.e., $H^+ + OH^- \rightleftharpoons H_2O$ (the symbol $\rightleftharpoons$ indicates equilibrium), whereby we multiply this formula with the same stoichiometric coefficient as that of the hydrogen ion (H^+) in the half-reaction under acidic conditions. By subsequently placing the hydrogen ions of the resultant autoionization formula at the *opposite* side in the half-reaction of where the hydrogen ions are positioned, all the hydrogen ions cancel out and we become the half-equation under basic conditions.

In a next example, we wish to balance the half-reaction that describes the evolution from the dichromaton ion ($Cr_2O_7^{2-}$) into the chromium(III) ion (Cr^{3+}) under *acidic conditions*. These are the steps that provide the appropriate half-equation for this reduction reaction (it is an example of *reduction*, as there is a gain of electrons):

- Step 1: Write the crude half-reaction
  $Cr_2O_7^{2-}(aq) \longrightarrow Cr^{3+}(aq)$
- Step 2: Balance the major elements
  $Cr_2O_7^{2-}(aq) \longrightarrow 2\,Cr^{3+}(aq)$
- Step 3: Balance the oxygen atoms
  $Cr_2O_7^{2-}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$ (3.10)
- Step 4: Balance the hydrogen atoms
  $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$
- Step 5: Balancing the electric charges gives the half-equation
  $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$

In the following example, we want to balance a half-reaction whereby the permanganate(VII) ion (MnO_4^-) is reduced to the manganese(II) ion (Mn^{2+}) in *basic conditions*. These steps deliver the desired half-equation:

- Step 1: Write the crude half-reaction

  $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

- Step 2: Balance the major elements

  $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq)$

- Step 3: Balance the oxygen atoms

  $MnO_4^-(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$

- Step 4: Balance the hydrogen atoms

  $MnO_4^-(aq) + 8\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$

- Step 5: Balance the electric charges

  $MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$

- Step 6: Adjust the autoionization formula of water

  $8\,H^+ + 8\,OH^- \rightleftharpoons 8\,H_2O$

- Step 7: Incorporate the autoionization formula into the half-reaction

  $MnO_4^-(aq) + \cancel{8\,H^+(aq)} + 5\,e^- + 8\,H_2O(l) \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l) + \cancel{8\,H^+(aq)} + 8\,OH^-(aq)$

- Step 8: Rearranging the water molecules gives the final half-reaction

  $MnO_4^-(aq) + 4\,H_2O(l) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 8\,OH^-(aq)$

(3.11)

3.4 State of Equilibrium

All the chemical equations mentioned so far have one aspect in common: they all assume that their reaction goes to full completion. That is, all the reactants transform entirely into products. However, more often than not, chemical reactions do not always proceed to completion. This is the case, for instance, for **reversible reactions**, whereby the reactants not only convert into products (the *forward reaction*) but the products simultaneously transform back into the reactants (the *reverse reaction*). An example is the reaction of hydrogen gas (H_2) with iodine vapour (I_2), forming hydrogen iodide (HI) in the process:

$$\begin{cases} \text{The reversible reaction:} & H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \\ \text{The forward reaction:} & H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \\ \text{The reverse reaction:} & 2\,HI(g) \longrightarrow H_2(g) + I_2(g) \end{cases} \tag{3.12}$$

After some time, both the forward and the reverse reaction reach an **equilibrium**, whereby the rate of both reactions is equal to each other. A necessary condition for achieving such chemical balance is that the reversible reaction must take place in the setting of a *closed system*, i.e., both the reactants and the products are kept in sealed spaces (they cannot escape).

Another example of a reaction in chemical equilibrium is that between the hexaquacobalt(II) cation ($Co(H_2O)_6^{2+}$) and the chloride anion (Cl^-), on the one hand, and the tetrachlorocobalt(II) anion ($CoCl_4^{2-}$) and water (H_2O), on the other hand:

$$\mathrm{Co(H_2O)_6}^{2+}(aq) + 4\,\mathrm{Cl}^-(aq) \rightleftharpoons \mathrm{CoCl_4}^{2-}(aq) + 6\,\mathrm{H_2O}(l) \tag{3.13}$$

At what point the equilibrium settles depends on a number of factors, including the concentration C of the reactants and products, the pressure p, and the temperature T. One guiding principle hereby is called **Le Chatelier's principle**, which states that, upon a perturbation of the closed system in terms of C, T, or p, the reversible reaction evolves in the direction that *counteracts* the perturbation.

Regarding a change in the **concentration C** of a particular molecule (the concentration of a molecule or atom is represented by square brackets), suppose that in our example 3.13 the concentration of the tetrachlorocobalt(II) ion ($[CoCl_4^{2-}]$) is *increased.* Le Chatelier's principle tells us that the system subsequently evolves in the direction that opposes this increase. In other words, the rate of the *reverse* reaction *goes up*, since in this way tetrachlorocobalt(II) is being reacted away into hexaquacobalt(II) and chloride. The same effect would be witnessed if the concentration of, for instance, chloride ($[Cl^-]$) is *diminished.* In contrast, *augmenting* the concentration of the hexaquacobalt(II) compound ($[Co(H_2O)_6^{2+}]$) would result in a *boosted* rate of the *forward* reaction.

When it comes to a change in the **pressure p**, let's say, a *decrease* in p, it follows from the ideal gas law ($pV = nRT$; see section 4.4.1) that at a constant temperature the volume of the closed system *expands.* As a result, the number of particles per unit of volume, i.e., the density, goes *down.* As per Le Chatelier's principle, the rate of the *forward* reaction is *enhanced*, as the total number of particles at the product side of the reversible reaction—add the stoichiometric coefficients together: $1 + 6 = 7$—is *larger* than that at the reactant side ($1 + 4 = 5$). Similarly, *raising* the pressure pushes up the density, which in turn ensures that the rate of the *reverse* reaction is *reinforced.*

Concerning a perturbation in the **temperature T** of the system, it is first and foremost essential to establish whether the forward reaction gives off heat to its surrounding, i.e., *exothermic*, or extracts heat from it, i.e., *endothermic.* In the case that the forward reaction is, for instance, exothermic, it then follows that the reverse reaction is endothermic. In our example 3.13, the forward reaction is *endothermic.* Therefore, if the system experiences a *decrease* in temperature, the rate of the *reverse* reaction, which is exothermic, is *increased*, according to Le Chatelier's principle. By the same logic, *boosting* the temperature *pushes up* the rate of the *forward* reaction.

4 Quantitative Chemistry

4.1 The Mole and the Relative Molar Mass

As there are unfathomably many atoms and molecules within fluids (i.e., liquids and gases) and solids, a specially designed quantity is conveniently put to use in chemistry to make calculations more transparent. That quantity is called the **mole** and is expressed in mol, whereby 1 mol is equal to the number of particles that are contained in 12 g of the carbon nuclide $^{12}_{6}C$, i.e., 6.022×10^{23}, which is known as **Avogadro's number N_A**. Put differently, the number of moles of a certain atom or molecule represents the amount of that atom or molecule.

For example, 0.5 moles of hydrogen sulfide gas (H_2S) contains 3.011×10^{23} H_2S compounds. To give another example, the amount of reactants in chemical equation 3.13 consists of 1 mole of the hexaquacobalt(II) compound and 4 moles of chloride.

From this definition, it is inferred that $\frac{1}{12}$ of one $^{12}_{6}C$ atom has a mass of $\frac{1}{N_A}$ g or $m_{(\frac{1}{12})} = 1.6606 \times 10^{-24}$ g, which is precisely how 1 atomic mass unit (*amu*) is defined (see section 1.3). In other words, 1 *amu* is equivalent to 1 $g \cdot mol^{-1}$.

Having said that, we can now look at the concept of the **relative molar mass M_r**, which is defined as the relative atomic mass A_r of a chemical element—remember that A_r is unitless (see Equation 1.3 of section 1.4)—expressed in units of grams per mol ($g \cdot mol^{-1}$). In other words, the molar mass M_r is *numerically equal* to the relative atomic mass A_r:

$$M_r = A_r \quad (\text{in } g \cdot mol^{-1}) \tag{4.1}$$

For instance, given that the relative atomic mass of lithium equals $A_r(Li) = 6.92$, its relative molar mass is then defined as $M_r = 6.92\ g \cdot mol^{-1}$.

In the case of **molecules**, the definition of the relative molar mass M_r remains the same, except that the relative atomic mass A_r is replaced by the relative *molecular* mass (a.k.a. molecular weight), which is the sum of all the relative atomic masses A_r of the individual elements of the molecule. For example, the relative molecular mass of hydrobromic acid (HBr) is equal to $[(A_r(H) = 1.01) + (A_r(Br) = 79.90)] = 80.91$, so that $M_r(HBr) = 80.91\ g \cdot mol^{-1}$.

A closer inspection at definition 4.1 reveals that the mass (in g) of a certain chemical substance can be found by multiplying the relative molar mass M_r by the number of moles of that substance. The relationship between these three entities can be formulated mathematically as follows:

$$n = \frac{m}{M_r} \quad (\text{in } mol) \tag{4.2}$$

This means that for **1 mole of a substance** its mass corresponds to the relative molar mass M_r expressed in g. Let us consider a couple of examples: given that M_r for aluminum phosphate ($AlPO_4$) is equal to $M_r(\text{AlPO}_4) = [(A_r(Al) = 26.98) + (A_r(P) = 30.79) + 4 \times (A_r(O) = 16.00)]$ g $\cdot\, mol^{-1} = 121.77$ g $\cdot\, mol^{-1}$, a mass of 20.4 g of this substance contains an amount of 0.168 mol (or a number of 0.168 moles); an amount of 6.23 mol of magnesium fluoride (MgF_2) has a mass of 388 g (with $M_r(Mg) = 24.31$ g $\cdot\, mol^{-1}$ and $M_r(F) = 19.00$ g $\cdot\, mol^{-1}$); and finally, a mass of 0.5 g of calcium aluminosilicate ($Al_2CaO_8Si_2$) comprises a number of 1.80×10^{-3} moles (with $M_r(Ca) = 40.08$ g $\cdot\, mol^{-1}$ and $M_r(Si) = 28.09$ g $\cdot\, mol^{-1}$).

4.2 Mass Percent and the Empirical Formula

Based on definition 4.1, it is possible to calculate the **mass percent composition (m-%)** of the individual elements within a compound, which is defined as:

$$m\text{-}\%\ (element\ x) = \left(\frac{\text{Total mass of } x \text{ in 1 mole of the compound}}{M_r(compound)}\right) \times 100 \text{ (in \%)} \qquad (4.3)$$

For instance, in the case of 1 mole of carbon chloride (CCl_4), whereby $M_r(C) = 12.01$ g$\cdot mol^{-1}$ and $M_r(Cl) = 35.45$ g $\cdot\, mol^{-1}$, the mass of each individual element is equal to $m_C = 12.01$ g and $m_{Cl} = 4 \times 35.45$ g $= 141.8$ g, and the relative molar mass of the compound is $M_r(\text{CCl}_4) = 153.81$ g (for 1 mole). Therefore, m-%(C) $= (\frac{12.01\ g}{153.81\ g}) \times 100 = 7.80\%$ and m-%(Cl) $= (\frac{141.8\ g}{153.81\ g}) \times 100 = 92.19\%$.

Sometimes the opposite problem arises whereby it is asked to identify the **molecular formula** of a substance when only the mass percent composition m-% of the individual elements of the compound is provided. To be able to complete this task, it is necessary to first set up the **empirical formula** of the compound, which is the formula that reflects the *ratio* of the individual elements within the compound. Bear in mind that this ratio must be expressed by integer values and be as small as possible, and that these values do *not* represent the stoichiometric coefficients, i.e., the number of moles of each element.

For instance, the *empirical formula* for dinitrogen tetroxide (N_2O_4) is NO_2, which implies a ratio of nitrogen to oxygen of 1:2. That is, for every nitrogen atom there are two oxygen atoms present (which does not mean that there is only 1 nitrogen atom present in the molecular formula of the compound).

Let us consider the example whereby we wish to find the molecular formula for chrysotile asbestos, given that the mass percent composition of its constitutive elements is 26.31% magnesium (Mg), 20.27% silicon (Si), 1.45% hydrogen (H), and 51.96% oxygen (O). The respective values of the relative atomic mass A_r for these elements are mentioned above in the previous examples.

In a first step, we convert these percentages to masses by considering a compound mass of 100 g, which means that $m_{Mg} = 26.31$ g, $m_{Si} = 20.27$ g, $m_H = 1.45$ g, and $m_O = 51.96$ g. Next, we calculate the amount of mol per element with the assistance of Equation 4.2, which gives us $n_{Mg} = 1.082$ mol, $n_{Si} = 0.722$ mol, $n_H = 1.436$ mol, and $n_O = 3.248$ mol. Now, we express these amounts as a ratio relative to the element with the *lowest* number of moles, i.e., silicon. This gives us the following ratios: Mg to Si with a value of 1.5:1, H to Si with a value of 2:1, and O to Si with a value of 4.5:1. As ratios must be written in terms of the smallest possible integer values, they become 3:2 (Mg to Si), 2:1 (H to Si), and 9:2 (O to Si). We then use these ratios to write the empirical formula for chrysotile asbestos, which becomes $Mg_3Si_2H_4O_9$.

Finally, if the relative molar mass M_r of the compound is provided, we can write up the molecular formula by multiplying the coefficients of the empirical formula by the ratio $\left(\frac{M_r(compound)}{M_r(empirical formula)}\right)$. If it is given that $M_r(compound) = 277.11\ g \cdot mol^{-1}$, and having calculated that $M_r(empirical formula) = [(3\times24.31)+(2\times28.09)+(4\times1.01)+(9\times16)]\ \mathrm{g}\cdot mol^{-1} = 275.33\ g \cdot mol^{-1}$, this results in a ratio of 1, which means that the molecular formula is identical to the empirical formula, which completes our exercise.

4.3 Masses and Chemical Equations

Equation 4.2 can also be applied to figure out the masses of reactants and products in balanced chemical equations. Let us use the balanced chemical equation of Example 3.5 whereby 2 moles of nitric acid (HNO_3) react with 1 mole of strontium hydroxide ($Sr(OH)_2$) to form 2 moles of water (H_2O) and 1 mole of strontium nitrate ($Sr(NO_3)_2$):

$$2\,\mathrm{HNO_3}(aq) + \mathrm{Sr(OH)_2}(aq) \longrightarrow 2\,\mathrm{H_2O}(l) + \mathrm{Sr(NO_3)_2}(aq) \tag{4.4}$$

In this equation, 2 moles of nitric acid corresponds to a mass of $m_{\mathrm{HNO_3}} = 2 \times (1.01 + 14.01 + 3 \times 16)\ \mathrm{g} = 126.04\ \mathrm{g}$ (whereby $M_r(N) = 14.01\ \mathrm{g} \cdot mol^{-1}$), 1 mole of strontium hydroxide with $m_{\mathrm{Sr(OH)_2}} = 1 \times (87.62 + 2 \times (16 + 1.01))\ \mathrm{g} = 121.64\ \mathrm{g}$ (whereby $M_r(Sr) = 87.62\ \mathrm{g} \cdot mol^{-1}$), 2 moles of water with $m_{\mathrm{H_2O}} = 2 \times (2 \times (1.01) + 16)\ \mathrm{g} = 36.04\ \mathrm{g}$, and 1 mole of strontium nitrate with $m_{\mathrm{Sr(NO_3)_2}} = 1 \times (87.62 + 2 \times (14.01 + 3 \times 16))\ \mathrm{g} = 211.64\ \mathrm{g}$.

In order to check whether our calculations are correct, we can apply the law of conservation of mass (see section 3.3). That is, the total sum of the masses of the reactants must match that of the products, or $126.04\ \mathrm{g} + 121.64\ \mathrm{g} = 36.04\ \mathrm{g} + 211.64\ \mathrm{g}$, which is indeed the case.

In the above example, the entire amount of both reactant masses completely reacts away, as their ratio corresponds to the stoichiometric ratio, i.e., the ratio of the stoichiometric coefficients of the reactants. However, this is not always the case. Often, one of the reactants is entirely consumed by the chemical reaction, while not all of the mass of the other reactant is used up. The *former reactant* is called the **limiting reactant**, and thus determines how much of the mass of the other reactant is spent.

Consider the balanced chemical reaction below whereby 1 mole of calcium carbide (CaC_2) is mingled with 2 moles of water (H_2O) and is transformed into 1 mole of calcium hydroxide ($Ca(OH)_2$) and 1 mole of ethyne gas (C_2H_2). We will look at the following question: If 100 g of each reactant is brought together, how much ethyne (in g) is produced at the end of the chemical reaction?

$$\mathrm{CaC_2}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{C_2H_2}(g) \tag{4.5}$$

In a first step, we determine the amount of mol of each reactant: $n_{\mathrm{CaC_2}} = \frac{100\ g}{(40.08+2\times12.01)\ g\cdot mol^{-1}}$ $= 1.56$ mol and $n_{\mathrm{H_2O}} = \frac{100\ g}{(2\times1.01+16)\ g\cdot mol^{-1}} = 5.55$ mol. Given that for every 1 mole of calcium carbide 2 moles of water is required, it follows then that for $n_{\mathrm{CaC_2}} = 1.56$ mol an amount of $2 \times 1.56 = 3.12$ mol of water is used, leaving thereby a leftover amount of $n_{\mathrm{H_2O},\ leftover} = (n_{\mathrm{H_2O},\ initial} - n_{\mathrm{H_2O},\ used}) = (5.55 - 3.12)$ mol $= 2.43$ mol of water. This means that calcium carbide ($\mathrm{CaC_2}$) is the *limiting reactant*.

We can now determine the total mass of each element used at the reactant side of the chemical equation: $m_{Ca} = (1.56 \times 40.08)$ g $= 62.52$ g, $m_C = (1.56 \times (2 \times 12.01))$ g $= 37.47$ g, $m_H = (3.12 \times (2 \times 1.01))$ g $= 6.30$ g, and $m_O = (3.12 \times 16)$ g $= 49.92$ g.

To find the amount of ethyne produced (expressed in mass), we observe at the product side of the equation that all the carbon elements, i.e., 2 in total, but only half of all the hydrogen elements, i.e., 2 out of a total of 4, are contained within the molecular formula of ethyne ($\mathrm{C_2H_2}$). This means that the amount of mass of carbon and hydrogen present in ethyne equals $m_{C(in\ \mathrm{C_2H_2})} = m_C = 37.47$ g and $m_{H(in\ \mathrm{C_2H_2})} = \frac{m_H}{2} = \frac{6.30}{2}$ g $= 3.15$ g, respectively. The amount of ethyne produced in this reaction is therefore equal to $m_{total} = (37.47 + 3.15)$ g $= 40.62$ g.

A shorter way to arrive at that answer is by observing the *stoichiometric coefficients*. That is, since calcium carbide ($\mathrm{CaC_2}$) is the limiting reactant and the stoichiometric coefficient of both calcium carbide ($\mathrm{CaC_2}$) and ethyne ($\mathrm{C_2H_2}$) is equal to 1, it follows that the number of moles of ethyne produced is equal to $n_{\mathrm{C_2H_2}} = n_{\mathrm{CaC_2}} = 1.56$ mol. Given that $M_r(\mathrm{C_2H_2}) = 26.04\ \mathrm{g} \cdot mol^{-1}$, the mass of the generated amount of ethyne gas is then calculated as $m_{\mathrm{C_2H_2}} = n_{\mathrm{C_2H_2}} \times M_r(\mathrm{C_2H_2}) = 1.56 \times 26.04$ g $= 40.62$ g.

4.4 Volumes and Solutions

4.4.1 The Ideal Gas Law

When it comes to the behaviour of gases in particular, there is an equation that describes how it evolves over time and space, called the **ideal gas law**, whereby it is assumed that the constitutive particles (more about particle theory in section 15) are unencumbered by intermolecular forces (see section 6.6) and that particle collisions occur in a perfectly elastic fashion, i.e., they do not stick together. The ideal gas law takes the following form:

$$pV = nRT \tag{4.6}$$

with p the pressure that the gas carries out on the walls of the container in which it is stored (expressed in pascal (Pa)), V the volume (in cubic meters $\mathrm{m^3}$), n the number of moles (in mol), $R = 8.314\ \mathrm{Pa{\cdot}m^3{\cdot}K^{-1}{\cdot}mol^{-1}}$ the gas constant, and T the temperature (in Kelvin K). If we change the units of volume from $\mathrm{m^3}$ to liter (L)—remember that 1 L = 1 $\mathrm{dm^3}$—and those of pressure from Pa to atm—whereby 1 atm = 101,325 Pa—the gas constant then takes the value of $R = 0.0820$ atm·L·K^{-1}·mol^{-1}.

Equation 4.6 allows us to convert volume to moles, and vice versa. For example, at a temperature of 32°C and a pressure of 2.3 atm, we know that the number of moles of the respective gas in a volume of 0.5 L is equal to $n = \frac{pV}{RT} = \frac{2.3 \times 0.5}{0.0820 \times (32+273.16)}$ mol $= 0.0460$ mol.

Furthermore, it follows from Equation 4.6 that the **molar volume $\mathbf{V_m}$**, i.e., the volume per mol, remains the same *regardless of the specific type of gas under consideration*, given a certain pressure and temperature. For instance, at standard temperature and pressure (STP), i.e., T = 273.16 K (0°C) and p = 1 atm, and room temperature and pressure (RTP), i.e., T = 298.16 K (25°C) and p = 1 atm, the molar volume measures:

$$\begin{cases} V_m(STP) = \dfrac{R \cdot T}{p} = \dfrac{0.0820 \times 273.16}{1}\ L \cdot mol^{-1} = 22.4\ L \cdot mol^{-1} \\ V_m(RTP) = \dfrac{R \cdot T}{p} = \dfrac{0.0820 \times 298.16}{1}\ L \cdot mol^{-1} = 24.4\ L \cdot mol^{-1} \end{cases} \tag{4.7}$$

Let us consider an example whereby we wish to find the molecular formula of a gaseous compound made of phosphorus (P) and hydrogen (H). What we are given is the following information: In a volume of 1 L, the total mass of the compound is 2.80 g, of which 2.63 g pertains to phosphorus, and at the same pressure and temperature, a volume of 1 L of oxygen gas (O_2) has a mass of 1.36 g.

In a first step, Equation 4.2 tells us that $n_{O_2} = 0.0425$. Next, we know from Equation 4.7 that the molar volume of different gases under equal conditions is the same. This means that for equal volumes, their amount of mol is also the same: $V_{m,1} = V_{m,2} \Leftrightarrow \frac{1L}{n_{O_2}} = \frac{1L}{n_{compound}} \Leftrightarrow n_{O_2} = n_{compound} \Leftrightarrow n_{compound} = 0.0425$. In a next step, we calculate the number of particles per element in the compound: $n_P = \frac{2.63}{30.97}$ mol $= 0.0849$ mol, and $n_H = \frac{2.80-2.63}{1.01}$ mol $= 0.168$ mol. If we compare these numbers to $n_{compound} = 0.0425$, we then find that there are twice as many phosphorus particles and four times as many hydrogen particles relative to the number of compound particles, which means that the chemical formula is equal to P_2H_4.

4.4.2 Molarity and Solubility

When compounds are dissolved, the chemical substance that is being dissolved is referred to as the **solute**, whereas the substance in which the solute is dissolved is known as the **solvent**. The homogenous mixture of the solute and the solvent is called the **solution**. Based on these definitions, the **molar concentration or molarity c** can be described as the quantity that measures the concentration of a solute in a given solution:

$$c = \frac{n_{solute}}{V_{solution}} \quad (\text{in } mol \cdot L^{-1} \text{ or } mol \cdot dm^{-3}) \tag{4.8}$$

For instance, if it is assumed that seawater, i.e., the solution, contains 31 g of sodium chloride (NaCl), i.e., the solute, per liter, then the number of moles of the solute is equal to

$n_{solute} = \frac{31}{22.99+35.45}$ mol = 0.530 mol. Therefore, the molarity c of NaCl per liter seawater corresponds to $c_{(\mathrm{NaCl})} = 0.530$ mol·L^{-1}. In another example, we want to find the required mass of sulphuric acid (H_2SO_4) to make 750 mL of a solution with a molarity of 2 mol·L^{-1}. Based on Equation 4.8, we calculate that for a volume of 750 mL, the amount of mol of the solute is equal to $n_{solute} = c_{(\mathrm{H_2SO_4})} \times V_{solution} = 2 \times 0.750$ mol = 1.5 mol. Given that $M_r(\mathrm{H_2SO_4}) = 98.09$ g·mol^{-1}, we find a mass of $m_{\mathrm{H_2SO_4}} = 147.14$ g.

There is a limit to the amount of solute that can be dissolved in a solvent. At the moment that adding more solute to a solution does not lead anymore to the dissolution of the solute, then the maximum molar concentration of the solute is achieved for that given solution, which is then referred to as the **saturated solution**. For instance, there is a point when adding sugar (the solute) to your tea (the solvent) leads to the accumulation of sugar on the bottom, i.e., it does not dissolve anymore in your tea, as the mixture of dissolved sugar and tea (the solution) has reached its point of saturation.

Solubility is then defined as the maximum *amount of mass of a solute* that can be dissolved in a solvent, and is usually expressed either in grams of solute per 100 g of solvent or in grams of solute per 100 mL of solvent. Note that when the limit of solubility is reached, the molarity of the solute does not further increase when additional solute is incorporated within the saturated solution. Factors that can impact the solubility include temperature (a heated solvent has a higher solubility), pressure (higher pressure increases solubility), and the chemical composition (e.g., more sugar can be dissolved in water compared with salt).

For example, suppose that we mix 18.6 g of nickel(II) fluoride (NiF_2) with 545 g of water (H_2O) at a temperature of 20°C. We wish to find out whether this particular solution is saturated, and if so, what the amount of excess solute in the solution is. The additional information provided is that the solubility of NiF_2 at 20°C is equal to 2.56 g per 100 g of water. To find the solubility for the volume of our solution, we perform the following calculation: $\frac{2.56g\ \mathrm{NiF_2}\times 5.45}{100g\ \mathrm{H_2O}\times 5.45} = \frac{13.95g\ \mathrm{NiF_2}}{545g\ \mathrm{H_2O}}$. Since we have added an amount of 18.6 g of NiF_2 to our solvent, it follows that our created solution is saturated (18.6 g > 13.95 g) and the amount of excess solute is equal to $m_{excess} = (18.6 - 13.95)$ g = 4.65 g.

4.4.3 Titration

An application of Equation 4.8 is what is called **titration**, which is a technique used in laboratories to calculate the unknown molarity of a substance, called the *analyte*, by letting the analyte react with a known volume and molarity of a standard solution. This method is typically applied to reactions between acids and bases (see section 9), whereby it is required at the point of neutralization that *the number of moles of the acid is equal to that of the base.*

Let us consider an example. We want to find out what the molarity of phosphoric acid (H_3PO_4) is, if it takes 125 mL of calcium hydroxide ($Ca(OH)_2$) with a molarity of 8.32 mol·L^{-1} to neutralize 47.5 mL of H_3PO_4. In a first step, let us write up the balanced chemical equation:

$$2\,\mathrm{H_3PO_4}(aq) + 3\,\mathrm{Ca(OH)_2}(aq) \longrightarrow \mathrm{Ca_3(PO_4)_2}(s) + 6\,\mathrm{H_2O}(l) \tag{4.9}$$

As we know that the number of moles of the acid (H_3PO_4) must equal that of the base ($Ca(OH)_2$), it follows from Equation 4.8 that $n_{(H_3PO_4)} = c_{(Ca(OH)_2)} \times V_{(Ca(OH)_2)} = (8.32 \times 0.125)$ mol = 1.04 mol. However, from the chemical reaction 4.9, it is clear that the relationship between the acid and the base in terms of moles is not 1:1, but is rather represented by the equation $n_{(H_3PO_4)} = \frac{2}{3} \times n_{(Ca(OH)_2)}$. Taking this fact into account, the above calculation is therefore corrected as follows: $n_{(H_3PO_4)} = \frac{2 \times 1.04}{3}$ mol = 0.693 mol. The molarity for H_3PO_4 can now be calculated and is equal to $c_{(H_3PO_4)} = \frac{0.693}{0.0475}\ \text{mol} \cdot \text{L}^{-1} = 14.6\ \text{mol} \cdot \text{L}^{-1}$.

4.4.4 Percentage Yield

The mass of products delivered by a real-world chemical reaction does not always correspond to what is theoretically dictated by the chemical equation because of, among other factors, incomplete reactions, losses during transfers of substances, side reactions, and losses during purification stages. The efficiency of a chemical process is reflected by a quantity called the **percentage yield**, and is defined as:

$$Percentage\ yield = \frac{actual\ yield}{theoretical\ yield} \times 100 \quad \text{(in \%)} \tag{4.10}$$

Let us have a look at two examples. First, consider the below chemical reaction whereby 8.4 g of copper (Cu) reacts with nitric acid (HNO_3) to form 21.71 g of cupric nitrate ($Cu(NO_3)_2$), as well as some nitric oxide (NO) and water (H_2O). The amount of cupric nitrate made is lower than its theoretical value, because of some undesired side reactions. It is asked to calculate the percentage yield.

$$3\,\text{Cu}(s) + 8\,\text{HNO}_3(aq) \longrightarrow 3\,\text{Cu(NO}_3)_2(aq) + 2\,\text{NO}(g) + 4\,\text{H}_2\text{O}(l) \tag{4.11}$$

In a first step, we determine the number of moles in 8.4 g of copper, i.e., $n_{Cu} = 0.132$ mol (with $M_r(Cu) = 63.55$ g·mol^{-1}). As per the chemical reaction 4.11, the number of moles of cupric nitrate is the same as that of copper. Assuming that the entire amount of copper is reacted away, the theoretical amount of mass of cupric nitrate that can be extracted from this process is therefore equal to $m = 24.79$ g (with $M_r(N) = 14.01$ g·mol^{-1}). As a result, the percentage yield equals 87.57 %.

In the second example, titanium dioxide (TiO_2) reacts with carbon (C) and chlorine gas (Cl_2) to form titanium tetrachloride ($TiCl_4$) and some carbon dioxide (CO_2) at a percentage yield of 83.6 %. We wish to establish the minimum masses of TiO_2 and Cl_2 necessary to produce an actual mass of 33.5 g of $TiCl_4$. The balanced chemical equation looks as follows:

$$\text{TiO}_2(s) + \text{C(s)} + 2\,\text{Cl}_2(g) \longrightarrow \text{TiCl}_4(l) + \text{CO}_2(g) \tag{4.12}$$

Given a yield of 83.6 %, it follows from the definition that the predicted quantity of $\mathrm{TiCl_4}$ equals $m_{theoretical} = 40.07$ g, which corresponds to an amount of $n_{\mathrm{TiCl_4}} = 0.211$ mol (with $M_r(Ti) = 47.87$ g·mol^{-1}). Given equal stoichiometric coefficients, this is also the number of moles of $\mathrm{TiO_2}$, so that $m_{\mathrm{TiO_2}} = 16.87$ g. The number of moles for $\mathrm{Cl_2}$ is then equal to $n_{\mathrm{Cl_2}} = 2 \times 0.211$ mol $= 0.422$ mol, which implies a mass of $m_{\mathrm{Cl_2}} = 29.92$ g.

To check whether these numbers make sense, we can subject them to the law of conservation of mass. That is, the sum of the reactant masses must equal that of the product masses. Indeed, 16.87 g $(\mathrm{TiO_2}) + 2.53$ g $(C) + 29.92$ g $(\mathrm{Cl_2}) = 40.07$ g $(\mathrm{TiCl_4}) + 9.28$ g $(\mathrm{CO_2}) = 49.3$ g (with some minor rounding errors).

5 Oxidation and Reduction

5.1 Modern and Historical Perspectives

There are several ways to define the concepts of oxidation and reduction. In section 3.3, we looked at the most modern description that explains **oxidation** as the *loss of electrons* by an atom, ion, or molecule and the process of **reduction** as the *gain of electrons*. Moreover, such a view is particularly useful when considering the workings of electrochemical cells (see section 12).

Nonetheless, oxidation is historically also described as the gain of oxygen atoms or the loss of hydrogen atoms, whereas reduction entails the loss of oxygen atoms or the gain of hydrogen atoms. In the remainder of this chapter, we will work with the modern description, but before we move on, let us look at two examples that explain oxidation and reduction in terms of oxygen and hydrogen atoms.

In the first example, we consider the process of burning methane gas (CH_4), which gives carbon dioxide (CO_2) and water vapour (H_2O) as products. In this reaction, the carbon (C) atom is oxidized, since it connects with a higher number of oxygen atoms, i.e., a change from 0 to 2 oxygen (O) atoms:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g) \tag{5.1}$$

The other example envisages methanol (CH_3OH) being poured over a hot copper gauze, resulting in the formation of formaldehyde (CH_2O) and hydrogen gas (H_2). While the number of oxygen atoms remains unaltered, the production of formaldehyde is regarded as oxidation, given a loss of hydrogen (H) atoms with respect to methanol, i.e., the number of hydrogen (H) atoms declines from 4 to 2):

$$\mathrm{CH_3OH}(l) \longrightarrow \mathrm{CH_2O}(g) + \mathrm{H_2}(g) \tag{5.2}$$

5.2 Redox Reactions

Different examples in section 3.3 were provided to get familiar with identifying ionic half-equations that involve only oxidation (e.g., see example 3.7) or only reduction (e.g., see example 3.10)—from example 3.7 it becomes clear that oxidation does not necessarily involves the gain of oxygen atoms. Let us examine two additional half-reactions.

In below reaction, zinc (Zn) is *oxidized* into a zinc peroxide anion (ZnO_2^{2-}). Again, all the steps are given to arrive at the balanced half-equation for the oxidation reaction (in an acid environment).

- Step 1: Write the crude half-reaction
  $\mathrm{Zn}(s) \longrightarrow \mathrm{ZnO_2^{2-}}(aq)$
- Step 2: Balance the major elements
  $\mathrm{Zn}(s) \longrightarrow \mathrm{ZnO_2^{2-}}(aq)$
- Step 3: Balance the oxygen atoms (5.3)
  $\mathrm{Zn}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{ZnO_2^{2-}}(aq)$
- Step 4: Balance the hydrogen atoms
  $\mathrm{Zn}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{ZnO_2^{2-}}(aq) + 4\,\mathrm{H^+}(aq)$
- Step 5: Balancing the electric charges gives the half-equation
  $\mathrm{Zn}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{ZnO_2^{2-}}(aq) + 4\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}$

The half-reaction below is another example of a *reduction* process, whereby a hypochlorite anion ($\mathrm{ClO^-}$) is reduced to a chloride anion ($\mathrm{Cl^-}$) under acidic conditions.

- Step 1: Write the crude half-reaction
  $\mathrm{ClO^-}(aq) \longrightarrow \mathrm{Cl^-}(aq)$
- Step 2: Balance the major elements
  $\mathrm{ClO^-}(aq) \longrightarrow \mathrm{Cl^-}(aq)$
- Step 3: Balance the oxygen atoms (5.4)
  $\mathrm{ClO^-}(aq) \longrightarrow \mathrm{Cl^-}(aq) + \mathrm{H_2O}(l)$
- Step 4: Balance the hydrogen atoms
  $\mathrm{ClO^-}(aq) + 2\,\mathrm{H^+}(aq) \longrightarrow \mathrm{Cl^-}(aq) + \mathrm{H_2O}(l)$
- Step 5: Balancing the electric charges gives the half-equation
  $\mathrm{ClO^-}(aq) + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cl^-}(aq) + \mathrm{H_2O}(l)$

Reduction-oxidation or **redox reactions** are reactions that *simultaneously* involve oxidation and reduction processes. Apart from the examples 3.8 and 3.9 studied in section 3.3, below we discuss another redox reaction. Sodium iodide (NaI) is reacted with iron(III) sulfate ($\mathrm{Fe_2(SO_4)_3}$) to produce iodine ($\mathrm{I_2}$), iron(II) sulfate ($\mathrm{FeSO_4}$), and sodium sulfate ($\mathrm{Na_2SO_4}$):

- Step 1: Write the balanced chemical reaction

  $2\,\mathrm{NaI}(aq) + \mathrm{Fe_2(SO_4)_3}(aq) \longrightarrow \mathrm{I_2}(s) + 2\,\mathrm{FeSO_4}(aq) + \mathrm{Na_2SO_4}(aq)$

- Step 2: Write the net ionic equation

  $2\,\mathrm{I^-}(aq) + 2\,\mathrm{Fe^{3+}}(aq) \longrightarrow \mathrm{I_2}(s) + 2\,\mathrm{Fe^{2+}}(aq)$

(5.5)

- Step 3: Write the half-equation for iodine (oxidation)

  $2\,\mathrm{I^-}(aq) \longrightarrow \mathrm{I_2}(s) \quad \Rightarrow \quad 2\,\mathrm{I^-}(aq) \longrightarrow \mathrm{I_2}(s) + 2\,\mathrm{e^-}$

- Step 4: Write the half-equation for iron (reduction)

  $\mathrm{Fe^{3+}}(aq) \longrightarrow \mathrm{Fe^{2+}}(aq) \quad \Rightarrow \quad \mathrm{Fe^{3+}}(aq) + \mathrm{e^-} \longrightarrow \mathrm{Fe^{2+}}(aq)$

Note that in exercises an unbalanced redox reaction is usually provided, which is then asked to balance by means of writing up the balanced half-reactions. Let us consider such an example. Hydrogen peroxide ($\mathrm{H_2O_2}$) reacts with the permanganate(VII) ion ($\mathrm{MnO_4^-}$) to form manganese(II) ($\mathrm{Mn^{2+}}$) and oxygen gas ($\mathrm{O_2}$). Under acidic conditions, the following steps are taken:

- Step 1: Write the unbalanced equation

  $\mathrm{H_2O_2}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{O_2}(g)$

- Step 2: Write the balanced half-reaction for oxidation

  $\mathrm{H_2O_2}(aq) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}$

- Step 3: Write the balanced half-reaction for reduction

  $\mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)$ (5.6)

- Step 4: Balance the electrons

  $[\ \mathrm{H_2O_2}(aq) \longrightarrow \mathrm{O_2}(g) + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-}\ ]\times 5$

  $[\ \mathrm{MnO_4^-}(aq) + 8\,\mathrm{H^+}(aq) + 5\,\mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\,\mathrm{H_2O}(l)\ ]\times 2$

- Step 5: Combing the half-reactions gives the balanced redox reaction

  $5\,\mathrm{H_2O_2}(aq) + 2\,\mathrm{MnO_4^-}(aq) + 6\,\mathrm{H^+}(aq) \longrightarrow 2\,\mathrm{Mn^{2+}}(aq) + 5\,\mathrm{O_2}(g) + 8\,\mathrm{H_2O}(l)$

However, not all chemical reactions are redox reactions, as in the case of the double displacement reaction 3.4 or the neutralization reactions 3.5 and 3.6 in section 3.3, since no electrons are being gained or lost. Below is another example of such a **non-redox reaction** whereby sodium sulfate ($\mathrm{Na_2SO_4}$) reacts with barium chloride ($\mathrm{BaCl_2}$), producing thereby sodium chloride (NaCl) and barium sulfate ($BaSO_4$)—this is an example of a double displacement reaction. In step 4, we see that no electrons are lost or gained, as barium (sulfate) retains its charge of plus 2 (minus 2) in the compound barium sulfate.

- Step 1: Write the balanced chemical reaction

  $Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow 2\,NaCl(aq) + BaSO_4(s)$

- Step 2: Convert the chemical reaction into an ionic equation

  $2\,Na^+(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Na^+(aq) + 2\,Cl^-(aq) + BaSO_4(s)$

  (5.7)

- Step 3: Identify the spectator ions

  $\cancel{2\,Na^+(aq)} + SO_4^{2-}(aq) + Ba^{2+}(aq) + \cancel{2\,Cl^-(aq)} \longrightarrow \cancel{2\,Na^+(aq)} + \cancel{2\,Cl^-(aq)} + BaSO_4(s)$

- Step 4: Write the net ionic equation

  $SO_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow BaSO_4(s)$

5.3 Oxidation States

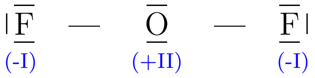
Before defining the oxidation state, we have to introduce another concept called **electronegativity**, which is described as the tendency of an atom to pull the bonding electrons within a chemical bond towards itself. Generally, the value of electronegativity for atoms increases as one moves up a Group in the Periodic Table and to the right in a given Period. As a consequence, elements at the right-hand side of the Periodic Table, such as non-metals and halogens, typically have a higher electronegativity relative to those elements at the left-hand side, i.e., metals, with fluorine (F) being the most electronegative element.

The **oxidation state (a.k.a. oxidation number)** is then defined as the electric charge the atoms of a molecule would possess in the hypothetical case that the electrons in every bond were allocated to the most electronegative element.

Let us consider the example of oxygen fluoride gas (OF_2). The two bonds in this molecule consist of 1 pair of electrons that is being *shared* between the atoms O and F (this type of bonding is called *covalent* bonding and is discussed in section 6.4). A pair of electrons is graphically represented by a line (—), and given that oxygen (O) has 6 valence electrons and fluorine (F) 7, the molecule OF_2 can be schematically depicted in the following way, which is called the *Lewis structure*:

$$|\overline{\underline{F}} \;—\; \overline{\underline{O}} \;—\; \overline{\underline{F}}| \tag{5.8}$$

Since F is more electronegative than O, it follows that in order to find the oxidation state of each element we assign the two bonding electrons in the two bonds to F. As a result, both F atoms gain one electron, whereas O loses two electrons (one at each side of the atom). This means that the hypothetical charge attributed to each element in this situation is *minus 1* for F and *plus 2* for O. These charges correspond to the oxidation numbers and are written in Roman numerals, i.e., -I and +II, respectively. In the below bonding structure of OF_2, the oxidation states are indicated in blue below the atoms:



$$\underset{\text{(-I)}}{|\overline{\underline{\mathrm{F}}}} \;—\; \underset{\text{(+II)}}{\overline{\underline{\mathrm{O}}}} \;—\; \underset{\text{(-I)}}{\overline{\underline{\mathrm{F}}}|} \tag{5.9}$$

This strategy can be applied to any molecule, and the following guidelines may help to establish the correct oxidation number for a specific atom:

1. The oxidation number of *free elements*, i.e., elements in their natural state, is *zero*. This applies both to the individual neutral elements (Mg, B, Al, etc.) and to polyatomic molecules made of the same element (e.g., O_2, O_3, N_2, S_8, H_2, and F_2).
2. For a given bond, the atom with the *higher (lower)* electronegativity value receives a *negative (positive)* oxidation state. In the case for instance of potassium sulfide (K_2S), the atom K has an oxidation number of +I, while S receives an oxidation state of -II.
3. Usually, the oxidation state of *alkali metals* is +I, for *alkaline earth metals* +II, and for *halogens* -I. For example, in the compound rubidium bromide (RbBr), the Rb atom (an alkali metal) has an oxidation number of +I, while that of Br (a halogen) is -I.
4. The order of electronegativity for the *atoms F, O, and Cl* is: $F > O > Cl$. As a result, although the oxidation state of oxygen in example 5.9 (OF_2) is +II, in the compound oxygen dichloride OCl_2 the atom O is allotted the oxidation number -II.
5. The oxidation state of an atom or a group of atoms in an *ionic compound* is equal to its *ionic charge*. For instance, for the ionic compound sodium nitrate ($NaNO_3$), the oxidation state of Na^+ and NO_3^- is +I and -I, respectively.
6. The *total sum* of the oxidation numbers of the atoms within an ion or molecule always corresponds to the amount of *net charge* of that ion or molecule. For example, the compound beryllium nitride (Be_3N_2) has a net charge of zero, so the individual oxidation numbers must also add up to zero. The element Be (an alkaline earth metal) has an oxidation state of +II, whereas the oxidation state of nitrogen is -III. Taking into account the number of atoms, this becomes: total sum oxidation numbers = (+II × 3) + (-III × 2) = 0.
7. The oxidation state of *hydrogen (H)* is typically equal to *+I*, except when it bonds with metals or the element boron (B), since its electronegativity is higher than that of metals. For example, in the compound calcium hydride (CaH_2), the alkaline earth metal calcium (Ca) has an oxidation number of +II, so that H receives an oxidation number of -I.
8. *Oxygen (O)* typically has an oxidation state of *-II*, except in the previously mentioned case of OF_2 (+II). What is more, when oxygen forms peroxides (O_2^{2-}), it obtains an oxidation number of -I. For example, in the case of zinc peroxide (ZnO_2), zinc is less electronegative than oxygen, so that Zn obtains an oxidation state of +II and O an oxidation number of -I. However, there is an exception for the compound dioxygen difluoride (O_2F_2), since F is more electronegative and thereby leaving oxygen with an oxidation state of +I.

9. The oxidation state of *any other element* is found by the number of electrons they would need when striving for the stable *octet structure*. For instance, the atom Al in the compound aluminum silicide (Al_4Si_3) has an oxidation state of +III, while the element Si has an oxidation number of -IV.

The oxidation state of an atom, ion, or molecule constitutes an alternative way by which oxidation and reduction reactions can be identified. **Oxidation** is then defined as the reaction through which the oxidation number of the respective substance *increases*, while the reaction that demonstrates a *decrease* in oxidation number makes up the **reduction** process.

Consider for example the unbalanced redox reaction of example 5.6, this time accompanied with the specified oxidation states:

$$\underset{\substack{\text{(H: +I)}\\\text{(O: -I)}}}{H_2O_2(aq)} + \underset{\substack{\text{(Mn: +VII)}\\\text{(O: -II)}}}{MnO_4^-(aq)} \longrightarrow \underset{\text{(+II)}}{Mn^{2+}(aq)} + \underset{\text{(0)}}{O_2(g)} \tag{5.10}$$

We observe in the above redox reaction 5.10 that the oxidation state of oxygen increases from -I (in H_2O_2) to 0 (in O_2), so that these two compounds make up the unbalanced half-reaction for oxidation. In contrast, the oxidation number of manganese decreases from +VII (in MnO_4^-) to +II (in Mn^{2+}), thereby identifying the unbalanced half-reaction for reduction. Note that the oxidation state of Mn in the compound MnO_4^- is equal to +VII, because the sum of the total hypothetical charge of O_4, i.e., -II×4 = -VIII, and the charge of Mn must be equal to the net charge of the ionic compound MnO_4^- (-I), which implies an oxidation number for Mn of +VII.

Some additional nomenclature is in place. In redox reactions, the reactant compound A, which takes part in the oxidation process and experiences an increase in oxidation number, is donating its electrons to reactant compound B, which is then subsequently being reduced and undergoes a reduction of its oxidation state. The compound A of the oxidation process is referred to as the **reducing agent**, whereas compound B of the reduction process is called the **oxidizing agent**.

For instance, in chemical equation 5.10, the compound H_2O_2 is giving up electrons, which are in turn used to reduce the compound MnO_4^-. As a result, H_2O_2 is designated the *reducing agent*. Similarly, as the permanganate(VII) ion MnO_4^- is stripping away electrons from hydrogen peroxide H_2O_2, and thereby oxidizing H_2O_2, the compound MnO_4^- is called the *oxidizing agent*.

Let us consider a final example for this section whereby we wish to balance a redox reaction based on the oxidation states of the respective atoms. Our example looks at the reaction when iron (Fe) is oxidized to form iron(III) oxide (Fe_2O_3). Step 1 reveals that Fe is the reducing agent, as it enables a reduction in the oxidation state of O_2 from 0 to -II. In contrast, O_2 takes up the role as oxidizing agent, since it is responsible for an increase in the oxidation number of Fe from 0 to +III. Note that the second line of step 7 is the result of the atoms Fe and O being able to react according to a ratio of 2:3.

- Step 1: Write the unbalanced equation

  $$\underset{(0)}{\mathrm{Fe}(s)} + \underset{(0)}{\mathrm{O_2}(g)} \longrightarrow \underset{\substack{(\mathrm{Fe:\ +III})\\(\mathrm{O:\ -II})}}{\mathrm{Fe_2O_3}(s)}$$

- Step 2: Write the unbalanced half-reaction for oxidation

  $$\mathrm{Fe}(s) \longrightarrow 2\,\mathrm{Fe}^{3+}(s)$$

- Step 3: Write the balanced half-reaction for oxidation

  $$2\,\mathrm{Fe}(s) \longrightarrow 2\,\mathrm{Fe}^{3+}(s) + 6\,\mathrm{e}^{-}$$

- Step 4: Write the unbalanced half-reaction for reduction

  $$\mathrm{O_2}(g) \longrightarrow 3\,\mathrm{O}^{2-}(g) \tag{5.11}$$

- Step 5: Write the balanced half-reaction for reduction

  $$3\,\mathrm{O_2}(g) + 12\,\mathrm{e}^{-} \longrightarrow 6\,\mathrm{O}^{2-}(g)$$

- Step 6: Balance the electrons

  $$[\ 2\,\mathrm{Fe}(s) \longrightarrow 2\,\mathrm{Fe}^{3+}(s) + 6\,\mathrm{e}^{-}\ ]\times 2$$

  $$[\ 3\,\mathrm{O_2}(g) + 12\,\mathrm{e}^{-} \longrightarrow 6\,\mathrm{O}^{2-}(g)\ ]\times 1$$

- Step 7: Combing the half-reactions gives the balanced redox reaction

  $$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 4\,\mathrm{Fe}^{3+}(s) + 6\,\mathrm{O}^{2-}(g)$$

  $$4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Fe_2O_3}(s)$$

5.4 Disproportionation

There is a specific class of redox reactions during which a compound A, which contains an atom X with a certain oxidation state, splits into two compounds B_1 and B_2, imparting thereby the atom X within the compound B_1 with a higher oxidation number and the atom X in B_2 with a lower oxidation state. This phenomenon is known as **disproportionation or dismutation**. Let us look at a couple of examples.

In a first example, hydrogen peroxide (H_2O_2) is disproportionated into water (H_2O) and oxygen gas (O_2). This reaction is usually very slow at room temperature, but evolves more quickly in the context of temperatures beyond 150°C or in the presence of a catalyst—this is a chemical substance that enhances the rate of the reaction (see section 10.4)—such as manganese(IV) oxide (MnO_2), platinum (Pt), or potassium iodide (KI).

$$2\,\underset{(\mathrm{O:\ -I})}{\mathrm{H_2O_2}(l)} \longrightarrow 2\,\underset{(\mathrm{O:\ -II})}{\mathrm{H_2O}(l)} + \underset{(0)}{\mathrm{O_2}(g)} \tag{5.12}$$

Redox reaction 5.12 reveals that the oxidation number of the oxygen atom both increases (in O_2) and decreases (in H_2O). This gives the following two balanced half-reactions (under acidic conditions):

$$\begin{cases} \text{Oxidation:} & H_2O_2(l) \longrightarrow O_2(g) + 2\,H^+(aq) + 2\,e^- \\ \text{Reduction:} & H_2O_2(l) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l) \end{cases} \tag{5.13}$$

In a next example, sodium hydrosulfite ($Na_2S_2O_4$) reacts with sodium hydroxide (NaOH) to form sodium sulfite (Na_2SO_3), sodium sulfide (Na_2S), and water (H_2O). This translates into the following balanced chemical equation:

$$3\,\underset{\text{(S: +III)}}{Na_2S_2O_4(aq)} + 6\,NaOH(aq) \longrightarrow 5\,\underset{\text{(S: +IV)}}{Na_2SO_3(aq)} + \underset{\text{(S: -II)}}{Na_2S(aq)} + 3\,H_2O(l) \tag{5.14}$$

Redox reaction 5.14 shows that the oxidation state of the element sulphur (S) augments from +III to +IV in the case of sodium sulfite and declines from +III to -II with respect to sodium sulfide. After converting the equation 5.14 into its net ionic equation form, the identification of the various oxidation states for sulphur allows us to write the following two balanced half-reactions (under basic conditions):

$$\begin{cases} \text{Oxidation:} & S_2O_4^{2-}(aq) + 4\,OH^-(aq) \longrightarrow 2\,SO_3^{2-}(aq) + 2\,H_2O(l) + 2\,e^- \\ \text{Reduction:} & S_2O_4^{2-}(aq) + 4\,H_2O(l) + 10\,e^- \longrightarrow 2\,S^{2-}(aq) + 8\,OH^-(aq) \end{cases} \tag{5.15}$$

In a third example, when nitrogen dioxide (NO_2) reacts with water, it is completely converted into nitric acid (HNO_3) and nitrous acid (HNO_2):

$$2\,\underset{\text{(N: +IV)}}{NO_2(g)} + H_2O(l) \longrightarrow \underset{\text{(N: +V)}}{HNO_3(aq)} + \underset{\text{(N: +III)}}{HNO_2(aq)} \tag{5.16}$$

From equation 5.16 we observe that NO_2 plays the role of oxidizing agent when it comes to HNO_3 as well as reducing agent relative to HNO_2. Considering the respective ionic compounds, we can write the two balanced half-reactions:

$$\begin{cases} \text{Oxidation:} & NO_2(g) + H_2O(l) \longrightarrow NO_3^-(aq) + 2\,H^+(aq) + e^- \\ \text{Reduction:} & NO_2(g) + e^- \longrightarrow NO_2^-(aq) \end{cases} \tag{5.17}$$

In a final example, upon heating of phosphorous acid (H_3PO_3) at a temperature of around 205-210°C, it decomposes with an approximate yield of 97 % into phosphoric acid (H_3PO_4) and the very toxic and inflammable phosphine gas (PH_3):

$$\underset{\text{(P: +III)}}{4\,H_3PO_3(s)} \longrightarrow \underset{\text{(P: +V)}}{3\,H_3PO_4(aq)} + \underset{\text{(P: -III)}}{PH_3(g)} \tag{5.18}$$

With the knowledge that the oxidation state of phosphorus (P) decreases from +III to -III with respect to phosphine gas and increases from +III to +V when it comes to phosphoric acid, we can construct the two balanced half-equations as follows:

$$\begin{cases} \text{Oxidation:} & H_3PO_3(s) + H_2O(l) \longrightarrow PO_4^{3-}(aq) + 5\,H^+(aq) + 2\,e^- \\ \text{Reduction:} & H_3PO_3(s) + 6\,H^+(aq) + 6\,e^- \longrightarrow PH_3(g) + 3\,H_2O(l) \end{cases} \tag{5.19}$$

6 Chemical Bonding

6.1 Substances and Mixtures

In this chapter, we focus our attention to the structure and properties of molecules and especially to the question of how their constitutive atoms bind together. In section 3.1, we looked at the distinction between **molecules** and **compounds**. We introduce here another concept, i.e., **mixture**, and also define **substance** as the common name for elements, compounds, or molecules.

While a compound is made of two or more different *elements* bound together, which can only break free from one another by way of *chemical* reactions, a mixture is a sample of matter that consists of two or more different *substances* blended together that can be separated from each other with the assistance of *physical* means, such as centrifugation, distillation, and filtration (see section 8.2 for more details).

Molecules possess properties that are *distinct* from those of their individual components, so that breaking them apart and reassembling them in a different composition chemically changes the original molecule, and thus effectively results in the creation of a new molecule. In contrast, the act of physically separating the substances in a mixture means that each substance maintains its intrinsic properties and does not lead to the formation of new substances.

What is more, mixtures can be classified as *homogenous*, i.e., the mixture shows only one identifiable state of matter, a.k.a. phase (see section 15.1 for a definition of the various states of matter), or as *heterogeneous*, i.e., more than one phase can be identified within the mixture.

Regarding the properties of substances, they can be placed under two broad categories: intensive and extensive properties. **Intensive properties**, on the one hand, are properties that are idiosyncratic to the substance and, as such, do not depend on the *amount* of the substance. They include density, melting point, boiling point, colour, odour, hardness, luster, temperature, and reactivity. On the other hand, **extensive properties** do rely on the amount present, such as volume, mass, weight, size, energy, and heat capacity.

6.2 General Characteristics of Bonding

The noble gases (Group 18 in the Periodic Table) are the most stable elements, since their electronic configuration is energetically the most favourable. For this reason, atoms usually prefer to form molecules in such a way so that it reflects this noble gas structure, also known as the **octet structure** (see also section 2.3 on trends in reactivity) or the **duplet structure**, in the case of helium (He). That is, when atoms come together to form a molecule, they tend to strive for an electronic configuration of their outer shell that resembles the one of noble gases, i.e., $1s^2$ for helium or $ns^2\ np^6$ for the other noble gases (with n the Period number, whereby $n \geq 2$).

Let us consider for instance the compound hydrogen chloride (HCl), whereby the electronic configuration of hydrogen (H) and chlorine (Cl) is $1s^1$ and $[Ne]\ 3s^2\ 3p^5$, respectively. As these elements bond covalently (see section 6.4), they *share* the two electrons within their bond. This allows hydrogen to attain the valence shell's electronic configuration of the noble gas helium ($1s^2$) and chlorine that of argon ($3s^2$ $3p^6$).

Another example is that of the ionic compound potassium bromide (KBr). The bond between both elements is ionic (see section 6.3), which implies that potassium (K) is *donating* an electron to bromine (Br). Given that the electronic configuration of K is equal to $[Ar]$ $4s^1$ and that of Br to $[Ar]$ $4s^2$ $3d^{10}$ $4p^5$, engaging in an ionic bond allows both elements to achieve an octet structure in their valence shell, i.e., the potassium cation K^+ that of argon ($3s^2$ $3p^6$), and the bromine anion Br^- that of krypton ($4s^2$ $4p^6$).

There exist three major types of chemical bonding between atoms, which underpin the formation of molecules: covalent bonding, ionic bonding, and metallic bonding. **Covalent bonds** are bonds among *non-metals* whereby pairs of electrons are shared, as in the case of diamond (C), water (H_2O), or nitric oxide (NO). The other two types of bonds rely on electrostatic forces due to the difference in polarity. That is, while **ionic bonds** are generally formed between positively charged *metal ions* and negatively charged *non-metal ions* (e.g., the alkaline metal ion Na^+ and halogen F^- combine to create the compound sodium fluoride NaF), **metallic bonds** arise from the attraction between positively charged *metal atoms* and the free-roaming negatively charged bonding electrons within a metallic substance (this is the case for substances made of, for instance, copper (Cu) or tungsten (W)).

However, there is another intermediate type of intramolecular bonding called *polar covalent bonding*, which sits between ionic and covalent bonding and is only covered superficially in section 6.4. In the next three sections, the three main types of chemical bonds are examined in greater detail.

6.3 Ionic Bonding

6.3.1 The Main Concept

An ionic bond is established as a result of the **electrostatic attraction** between two ions with an opposite charge. One ion has a positive charge (the cation), which is typically a **metal ion**, as metals tend to exhibit weak electronegativity (see section 5.3). The other ion is negatively charged (the anion), and is usually represented by a **non-metallic element**, which displays higher electronegative values.

Due to their significant difference in electronegativity, which is underpinned by the concepts of ionization energy and electron affinity (see section 2.3), the metal ion transfers one or more electrons to the non-metal ion, whereupon the electrostatic force creates an ionic bond. The resulting molecular structure is called an *ionic compound*, and section 3.2 mentions some of the most common ones, including various compound ions, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-).

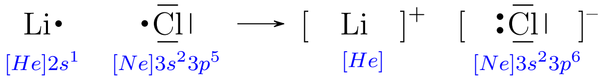
As already alluded to in section 6.2, the electronic configuration of elements can be of help to determine the charge of the respective ion. The **metals in Group 1 (Group 2)** have a configuration of [X] ns^1 ([X] ns^2), with X being the noble gas of the Period $n-1$. Stated another way, their *outer electron shell* has the general form of ns^1 and ns^2, respectively, with n the Period number. This means that these metals will give away one (Group 1) or two (Group 2) electrons from the s subshell of their valence shell—that is, their valence electrons—to engage in an ionic bond, so that the subsequent ions will show an *electric* *charge of plus 1 and plus 2*, respectively.

For example, the element lithium (Li) has a configuration of $[He]\ 2s^1$ and would donate 1 electron to achieve the duplet structure of helium (He) when forming an ionic bond. The cation of lithium would be written as Li^+ (a charge of plus 1). Another example is calcium (Ca) with an electronic structure of $[Ar]\ 4s^2$, so that it would give up 2 electrons to attain the octet structure of argon (Ar) and establish an ionic bond. In this case, the cation is formulated as Ca^{2+} (a charge of plus 2).

With respect to the **non-metals of Group 16 and the halogens of Group 17**, the configuration of their outer electron shell is of the form $ns^2\ np^4$ and $ns^2\ np^5$, respectively. In other words, the non-metals of Group 16 (the halogens of Group 17) will attract 2 electrons (1 electron) to completely fill their p subshell and obtain the stable configuration of the noble gas of their respective Period, obtaining thereby an *electric charge of minus 2 (minus 1).*

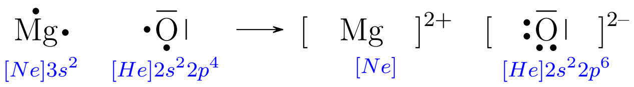
For example, the non-metal element sulphur (S) of the Group 16 with a structure of $[Ne]\ 3s^2\ 3p^4$ tends to attract 2 electrons, since it needs to add 2 electrons to its 6 valence electrons to achieve the octet structure of the noble gas argon (Ar). The sulphur anion is written as S^{2-}. A second example is the halogen iodine (I) with an electron configuration of $[Kr]\ 5s^2\ 4d^{10}\ 5p^5$. It requires one additional electron to reflect the stable octet structure of the noble gas xenon (Xe), and its anion has the form I^-.

Let us consider the **Lewis diagram** of three ionic compounds to further illustrate how ionic bonds are formed. The first example is the compound lithium chloride LiCl, whereby an ionic bond is established between the alkali metal lithium (Li) and the halogen chlorine (Cl). As mentioned previously, Li has 1 valence electron, and as a metal, it will donate it to Cl, which has an electronic configuration of $[Ne]\ 3s^2\ 3p^5$ with 7 valence electrons. The Lewis diagram of the ionic bond between the two ions Li^+ and Cl^- is therefore the following:



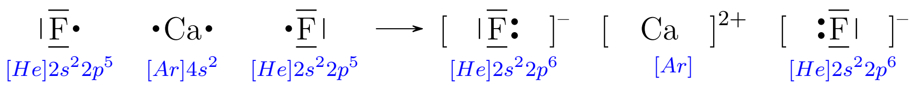
$$\underset{[He]2s^1}{\mathrm{Li}\bullet} \qquad \underset{[Ne]3s^23p^5}{\bullet\overline{\underline{\mathrm{Cl}}}|} \longrightarrow \left[\ \underset{[He]}{\mathrm{Li}}\ \right]^+ \quad \left[\ \underset{[Ne]3s^23p^6}{:\overline{\underline{\mathrm{Cl}}}|}\ \right]^- \tag{6.1}$$

The second example concerns the ionic compound magnesium oxide (MgO). The alkaline earth metal magnesium (Mg) and the non-metal oxygen (O) have an electronic configuration of $[Ne]\ 3s^2$ and $[He]\ 2s^2\ 2p^4$, respectively. This results in the following Lewis diagram:



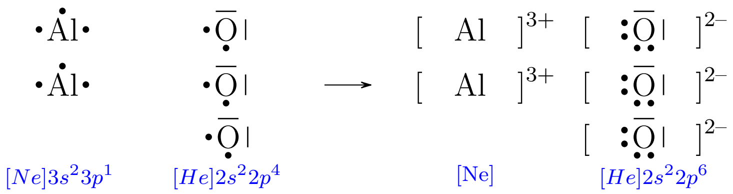
$$\underset{[Ne]3s^2}{\dot{\mathrm{M}}\mathrm{g}\bullet} \qquad \underset{[He]2s^22p^4}{\bullet\overline{\underset{\bullet}{\mathrm{O}}}|} \longrightarrow \left[\ \underset{[Ne]}{\mathrm{Mg}}\ \right]^{2+} \quad \left[\ \underset{[He]2s^22p^6}{:\overline{\underset{\bullet\bullet}{\mathrm{O}}}|}\ \right]^{2-} \tag{6.2}$$

The third example takes a metal of Group 2 and binds it with a halogen: the ionic compound calcium fluoride (CaF_2). In this case, the alkaline earth metal calcium (Ca) with an electron structure of $[Ar]\ 4s^2$ donates one electron to each fluorine (F) atom, which has the configuration $[He]\ 2s^2\ 2p^5$. The Lewis diagram becomes:



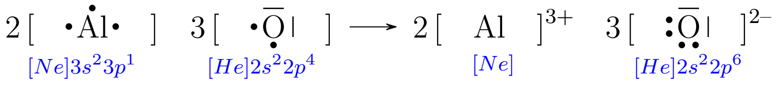
(6.3)

If we turn our attention for a moment to the metals of the category *other metals* (see the Periodic Table in Fig. 2.1) and take, for instance, the metal **aluminum (Al)** of Group 13 with an electron configuration of $[Ne]\ 3s^2\ 3p^1$, we see from the number of valence electrons that aluminum (Al) has the tendency to give away three electrons when engaging in an ionic bond, converting therefore into a cation with *charge plus 3* (Al^{3+}). In the event that it bonds with oxygen (O), whose ion is usually of the form O^{2-}, the ionic compound aluminum oxide (Al_2O_3) is created, which translates into the following Lewis diagram:



(6.4)

Or in a more simplified form, this can be written as:



(6.5)

6.3.2 Multiple Oxidation States

In case that an element takes on **various oxidation states** (see section 5.3), which typically occurs for the transition metals, the name of the ionic compound will mention between parentheses the oxidation number that the respective element adopts.

For instance, the ionic compound $FeBr_2$ is known as iron(II) bromide, whereas the name of $FeBr_3$ is iron(III) bromide. This implies that the charge of the iron cation is *plus 2* in $FeBr_2$ and *plus 3* in $FeBr_3$, since the bromine anion Br^- has a negative charge of minus 1 in both compounds. When turning to the element copper (Cu), the name of the compounds CuCl, CuF_2, $Cu(NO_3)_3$, and CuO_2 is copper(I) chloride, copper(II) fluoride, (the rare) copper(III) nitrate, and (the unstable) copper(IV) oxide, respectively. As a final example, if we consider the element vanadium (V), the ionic compounds VO_2 and V_2S_5 are named vanadium(IV) oxide and vanadium(V) sulfide, respectively.

Although it is less common, some *non-transition metals* may also exist in various oxidation states to form different ionic compounds. For instance, while aluminum (Al) is usually associated with oxidation state +III (e.g., in aluminum(III) oxide or Al_2O_3), aluminum(II) oxide with a chemical formula of AlO has been detected in the composition of a number of stars. Similarly, whereas we would normally attribute an oxidation state of +II to the element calcium (Ca), it has been reported that the atmosphere of several stars contains calcium(I) chloride (CaCl).

What becomes apparent from the previous two paragraphs is that the chemical formula of an ionic compound can (most of the time) be identified when the charge of all the ions is known, bearing in mind that the total charge of the ionic compound must equal the sum of the individual charges of the ions. For instance, if we bring a potassium (K^+) and a sulphur ion (S^{2-}) together to form a neutral ionic compound, we can infer that we need two potassium ions in order to end up with a total net charge of zero. The chemical formula then becomes K_2S.

Let us consider some additional examples. If given a sodium cation (Na^+) together with a phosphate anion (PO_4^{3-}), we can deduce that they will form the ionic compound Na_3PO_4. If instead a magnesium cation (Mg^{2+}) is combined with a phosphate anion (PO_4^{3-}), then the resultant compound becomes $Mg_3(PO_4)_2$. By the same logic, a magnesium cation (Mg^{2+}) and a sulfate (SO_4^{2-}) anion turn into $MgSO_4$, an iron(III) cation (Fe^{3+}) and a nitrate anion (NO_3^-) into $Fe(NO_3)_3$, and a cesium cation (Cs^+) and an oxygen anion (O^{2-}) into Cs_2O.

6.3.3 Physical Properties

In terms of the **physical properties** of ionic compounds, let us have a look at five characteristics: hardness, melting point, boiling point, latent heat or enthalpy, and electrical conductivity.

Ionic compounds in aggregate form (i.e., many individual compounds put together) tend to combine in a regular pattern at atomic scales, which is called a crystal lattice, whereby cations are positioned next to the anions in a recurrent and alternating fashion.

Due to the strong electrostatic forces present throughout the lattice, ionic crystals show a **high degree of hardness**. If sufficient pressure is exerted upon the crystal, it will lead to a shift in the position of a layer of cations or anions and equal charges will now sit next to each other. The repulsive force subsequently ensures that the lattice breaks apart rather quickly. That is, even though ionic solids are hard, they are also **brittle**.

During the phase change of melting (i.e., the transition from a solid into a liquid phase) or vaporization (i.e., the change from a liquid into a gaseous state), a certain amount of energy is required—this energy is called the *latent heat of fusion or enthalpy of fusion* and the *latent heat of vaporization or the enthalpy of vaporization*, respectively—to severe the inter-molecular bonds (see section 6.6 and section 15.2) between the ionic compounds. Since the electrostatic force is strong, a relatively **high enthalpy of fusion and vaporization** is needed to complete the stage of melting and vaporization of the ionic crystal.

The strength of the electrostatic force also explains why a lot of energy is required to bring a solid (a liquid) *up to* its melting point (boiling point). In other words, ionic compounds have **high melting and boiling points**. Table 6.1 illustrates these two characteristics for a number of ionic crystals.

Table 6.1: The melting and boiling points of various ionic compounds

Ionic Compound	Melting Point (in °C)	Boiling Point (in °C)
$AlPO_4$	1,800	/
CaF_2	1,418	1,533
$FeBr_2$	684	934
KCl	771	1,420
K_2S	840	912
K_2SO_4	1,069	1,689
LiCl	613	1,383
MgO	2,830	3,600
NaCl	801	1,413
NH_4NO_3	169.7	210

Finally, ionic crystals also have the ability to be a conduit for the flow of electricity, a property known as **electrical conductivity**. However, they only conduct electricity when either in a *melted* phase or when a solid is *dissolved* in an aqueous solution, because in these physical states the dissociated cations and anions are able to freely move around and connect with the respective electrode of the electrochemical cell (see section 3.3 and 12). In contrast, in ionic solids, the ions remain in a fixed position within the crystal lattice, unable to wander about and make a connection with the electrodes, and do therefore not conduct any current. Stated differently, ionic solids make good insulators.

6.4 Covalent Bonding

6.4.1 The Main Concept

A second major type of chemical bonds is known as the **covalent bond**, which is a bond between *non-metallic elements* whereby one or more pairs of valence electrons—called bonding or binding electrons—are shared among the atoms in an approximately equal fashion. Depending on whether one, two, or three pairs of valence electrons are shared, the covalent (molecular) compound contains a **single, double, or triple bond**, respectively.

It follows from this definition that the difference in electronegativity for all the molecules that are not compounds—in other words, the molecules that are made of two or more atoms of the *same* element (see section 3.1)—is equal to *zero*. For example, the molecule iodine (I_2) consists of two iodine atoms each with an electronegativity of 2.66, so that the difference is equal to $2.66 - 2.66 = 0$. Bearing in mind the octet rule, the Lewis structure for I_2, with a total of 14 valence electrons, shows a *single bond* between the atoms:

$$|\overline{\underline{\mathrm{I}}} \;-\; \overline{\underline{\mathrm{I}}}| \tag{6.6}$$

Another example is the oxygen molecule (O_2), whereby the total of 12 valence electrons results in the formation of a *double bond*:

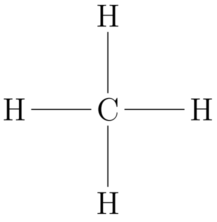
$$\langle \mathrm{O} \;=\; \mathrm{O} \rangle \tag{6.7}$$

A third example demonstrates the presence of a *triple bond* in nitrogen gas (N_2), due to a total of 10 valence electrons:

$$|\mathrm{N} \equiv \mathrm{N}| \tag{6.8}$$

In contrast to the ionic bond, the difference in electronegativity (ΔEN) between the elements that participate in the covalent bond is much smaller, i.e., typically lower than a value of $\Delta\mathrm{EN} = 1.7$. More accurately, the difference in electronegativity for the **polar covalent bond**—this is a covalent bond with a pronounced ionic character and is not further discussed in detail in this preparation course; see also section 6.2—usually ranges between $\Delta\mathrm{EN} = 0.4$ and $\Delta\mathrm{EN} = 1.7$, whereas for the **non-polar covalent bond** the difference lies roughly between $\Delta\mathrm{EN} = 0$ and $\Delta\mathrm{EN} = 0.4$. Notwithstanding this numerical threshold between polar and non-polar covalent bonds, the geometrical structure of the molecular compound also plays a role in determining whether a bond is polar or non-polar in nature.

For example, the non-polar molecular compound methane (CH_4) is held together by four covalent bonds between the non-metal element carbon (C) and the four non-metal elements hydrogen (H)—note that the difference in electronegativity between C and H is equal to $\Delta\mathrm{EN} = 0.35$—and shows the following Lewis structure:

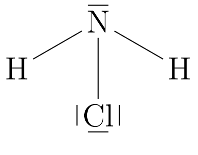


$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & — & \mathrm{C} & — & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array} \tag{6.9}$$

A second example of a non-polar molecule is carbon dioxide (CO_2). Even though the difference in electronegativity between the carbon (C) and the oxygen (O) atom measures ΔEN = 0.89, it is still a non-polar covalent compound, since its structure is linear and symmetrical. The Lewis structure of CO_2 takes the following form:

$$\langle \mathrm{O} = \mathrm{C} = \mathrm{O} \rangle \tag{6.10}$$

An example of a polar covalent compound is chloramine (NH_2Cl), whose Lewis structure can be drawn as follows:



(6.11)

Other polar molecular compounds include water (H_2O), ammonia (NH_3), nitrogen dioxide (NO_2), iodine monobromide (IBr), and phosphorus trifluoride (F_3P)—see also section 3.2 for more examples of covalent molecules.

6.4.2 Giant Covalent Structures

All of the above-mentioned molecular compounds are rather small in size and their covalent bonds are therefore weaker in strength relative to the typical ionic bonds. However, covalent bonding can equally occur in **giant covalent structures**, which are large networks of atoms covalently bound together, such as in the case of diamond, graphite or silicon dioxide. In contrast to the small covalent compounds, these giant structures *exceed* the strength of the ionic bonds.

Diamond consists of carbon (C) atoms covalently linked in a giant structure. As every C atom has four valence electrons, it forms four single bonds with other C atoms, and the resultant molecule adopts a tetrahedral geometry (i.e., the angles between the C atoms measures 109.47°). This pattern is repeated for every C atom throughout the giant structure, whereby the number of C atoms involved determines the size fo the solid crystal. A part of a diamond giant covalent structure is drawn in Fig. 6.1.

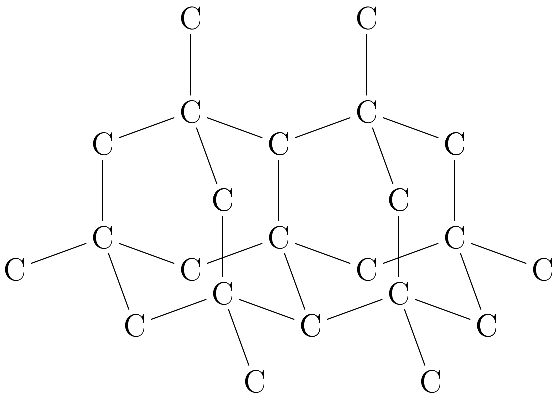


Figure 6.1: Part of the covalent solid network structure of diamond

Graphite is a carbon-based giant covalent structure that is made of large sheets of connected C atoms, called *graphene layers*, one stacked on top of the other. Within one sheet, each C atom is attached to three other C atoms, forming hexagonal rings with an angle of 120° between the atoms. The fourth valence electron is *moving freely* throughout the sheet. In fact, the ensemble of the free electrons provides additional bonding strength within one sheet due to the presence of intermolecular forces (see section 6.6), which is why *graphene* is *stronger* than diamond.

Intermolecular forces also exist *between* the layers and are as such responsible for holding them together—note that intermolecular bonds are weak, so that *graphite* as a whole is *weaker* than diamond. Fig. 6.2 shows the top view of one graphene layer within this crystalline solid of interlinked C atoms and illustrates its hexagonal character.

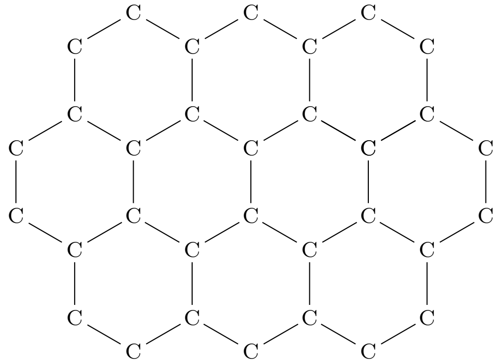


Figure 6.2: A graphene layer within the covalent giant network of graphite

The covalent giant network structure of **silicon dioxide** (SiO_2), also called silicon(IV) oxide or silica, is a solid, crystalline material with a similar tetrahedral geometry to that of diamond—after all, both silicon (Si) and carbon (C) belong to the same Group, i.e., Group 14. More concretely, silicon (Si) takes the place of the carbon (C) atom in diamond and between every two silicon (Si) atoms an oxygen (O) atom is positioned. Fig. 6.3 depicts a simplified form of the giant structure of silica (simplified, because the bond angle Si-O-Si is typically 145° instead of a straight line and each oxygen atom contains two lone electron pairs, which are not drawn).

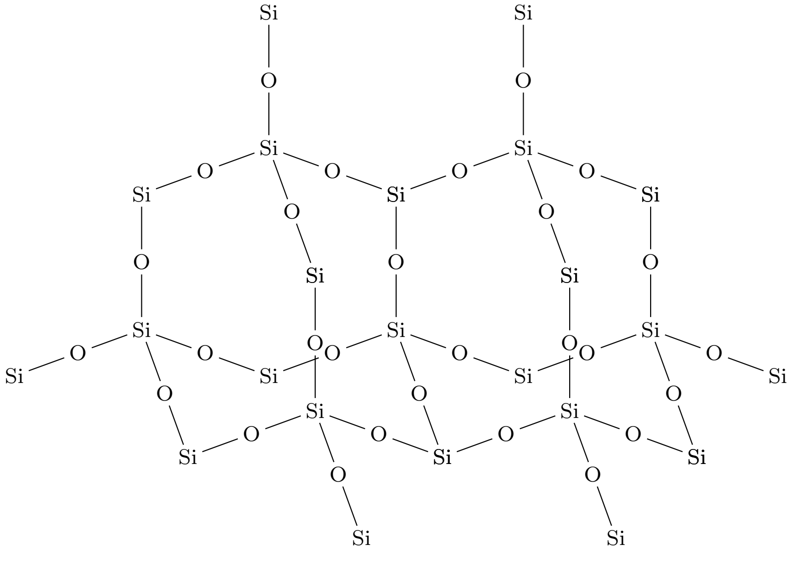


Figure 6.3: Part of the covalent network solid structure of silica

6.4.3 Physical Properties

Concerning the **physical properties**, the different types of *molecular compounds* can generally be written in terms of *increasing* **melting point** in the following order: small non-polar molecules (e.g., H_2 or F_2), larger non-polar compounds (e.g., CO_2 or CH_4), and polar compounds (e.g., H_2O or NO_2). In contrast to the smaller compounds, larger compounds tend to display *stronger intermolecular forces*, which push up the melting point. Due to these wide range of melting (and boiling) points, covalent compounds can exist in a solid, liquid, or gaseous state at room temperature, whereas *ionic compounds* only take on a solid form at these temperatures. Put differently, the melting point of ionic solids are much higher (see Table 6.1) due to their ability to reside in crystalline structures.

When it comes to *covalent networks*, their melting point is much higher still, as melting requires *breaking the covalent bonds*, which are stronger than the weak intermolecular bonds. Table 6.2 provides an overview of the melting point of various covalent compounds and giant structures.

Table 6.2: The melting points of different molecular compounds and network solids

Molecular Compound	**Melting Point (in °C)**	**Covalent Network Structure**	**Melting Point (in °C)**
H_2	-259.16	C_{60}	280
F_2	-219.67	SiO_2	1,713
CH_4	-182.4	SiC	2,730
F_3P	-151.5	Graphite	3,600
NH_2Cl	-66	Diamond	4,027
CO_2	-56.6		
NO_2	-11.2		
H_2O	0		
I_2	113.7		
$C_{12}H_{22}O_{11}$	185.5		

In addition to low melting (and boiling) points, *molecular compounds* possess 10 to 100 times *lower* values of **enthalpy of fusion and vaporization** with respect to their ionic counterparts. Regarding the characteristic of **hardness**, materials made of covalent compounds are overall *softer, more flexible, and easier to break* compared to matter based on ionic bonds. What is more, molecular compounds display *poor* **electrical conductivity**, since they dissolve into neutral molecules instead of charged ions. Finally, covalent compounds typically show a *reluctance* to be dissolved in water (with polar compounds showing a slightly higher solubility in water relative to non-polar compounds). As always, there are exceptions to these general characteristics. For example, glucose ($C_6H_{12}O_6$) and ethanol (C_2H_6O), which are both polar covalent compounds, dissolve quite well in water.

Covalent giant network structures share two of their characteristics with those of molecular compounds: they *refuse* to dissolve in water and are generally *poor* electrical conductors (good insulators). An exception is graphite, as it accommodates free-roaming electrons within its graphene sheets which assist in conducting a current.

However, covalent network solids are overall quite *hard* due to the presence of covalent bonds in a three-dimensional network. Again, graphite forms an exception here, since the various graphene sheets can easily move due to the weak intermolecular forces between them, so that graphite has a soft and slippery feel to it. Moreover, as a result of the spacing between the graphene layers, graphite usually exhibits a *lower density* compared to diamond (2,260 $kg \cdot m^{-3}$ versus 3,500 $kg \cdot m^{-3}$).

6.5 Metallic Bonding

6.5.1 The Main Concept

Whereas in ionic bonds the electrostatic force emerges in response to the presence of *static* electric charges (i.e., the electrons are bound to the ions), in **metallic bonds** the electrostatic force is manifested as a result of attractive interactions between **positively charged metal atoms** that are located in a **fixed position** in a lattice structure and **free-floating negatively charged electrons** scattered throughout the material. These bonding electrons are often collectively referred to as the *electron cloud*. In other words, the electrons are being shared among the metal atoms in the sense that they can hop from one atom to the next.

Bear in mind that the positively charged metal atoms are *not* ions, since the electrons are not lost to the atom, only being shared amongst other atoms.

Yet another way of formulating this feature of electrons being shared is saying that the electrons are *delocalized*. The *higher* the number of delocalized valence electrons, the *stronger* the metallic bond, since more electrons enhance the electrostatic attractive force between them and the positive nuclear charges of the metal atoms—keep in mind that other factors also impact the bond strength, including the size of the atom and intermolecular forces. This explains, for instance, why the transition metals have overall stronger metallic bonds than the alkali and alkaline earth metals—which combined are sometimes referred to as *light metals*—since the transition metals also engage the electrons of the *d* and *f* orbital (apart from the *s* orbital).

Examples of metallic crystals made of *pure metals* include copper (Cu), iron (Fe), aluminum (Al), lithium (Li), gold (Au), osmium (Os), and zirconium (Zr). Metallic bonding also occurs in *metal alloys* (see section 14.2.1), such as tungsten carbide, which is based on tungsten (W) and carbon (C), stainless steel, which is based on iron (Fe), chromium (Cr), carbon (C), and nickel (Ni), invar, which is based on nickel (Ni) and iron (Fe), and solder, which is based on tin (Sn), copper (Cu), lead (Pb), and antimony (Sb). Even *non-metallic materials* can exhibit metallic bonding characteristics, such as graphene in graphite (see section 6.4), whereby an electron cloud is dwelling among the carbon atoms, as well as hydrogen (H) at extremely high amounts of pressure.

6.5.2 Physical Properties

With regard to the **physical properties**, a higher number of electrons within the electron cloud (i.e., a higher electron density) leads to stronger bonds, as mentioned previously. This, in turn, results in a **harder** material and a *higher* **melting and boiling point**. For example, while metals from Group 1 melt under 200°C, (most of the) transition metals register a melting point above 1,000°C.

Table 6.3 illustrates in ascending order the melting point of various metals across the Periodic Table. It furthermore shows that, besides electron density, other factors, such as atom size, also influence the value of melting points.

For instance, the melting point *decreases* when moving *down Group 1 and Group 2*, as a larger atom implies a reduction in the strength of the electrostatic forces. However, down the Groups of the transition metals (except for Group 12), the melting point increases, as in addition to the *s* and *d* orbitals also the electrons of the *f* orbital become involved.

Table 6.3: The melting points of various metals

Metal	**Type**	**# Valence Electrons**	**Melting Point (in °C)**
Mercury (Hg)	Transition metal (G12)	2	-38.9
Gallium (Ga)	Other metal (G13)	3	29.7
Rubidium (Rb)	Alkali metal (G1)	1	39.3
Potassium (K)	Alkali metal (G1)	1	63.3
Sodium (Na)	Alkali metal (G1)	1	97.8
Lithium (Li)	Alkali metal (G1)	1	180.5
Tin (Sn)	Other metal (G14)	4	231.9
Lead (Pb)	Other metal (G14)	4	327.5
Zinc (Zn)	Transition metal (G12)	2	419.5
Tellurium (Te)	Metalloid (G16)	6	449.5
Antimony (Sb)	Metalloid (G15)	5	630.6
Magnesium (Mg)	Alkaline metal (G2)	2	649.8
aluminum (Al)	Other metal (G13)	3	660.3
Strontium (Sr)	Alkaline metal (G2)	2	776.8
Calcium (Ca)	Alkaline metal (G2)	2	841.8
Beryllium (Be)	Alkaline metal (G2)	2	1,278
Scandium (Sc)	Transition metal (G3)	3	1,540.8
Hafnium (Hf)	Transition metal (G4)	4	2,232.8
Iridium (Ir)	Transition metal (G9)	9	2,446
Tungsten (W)	Transition metal (G6)	6	3,421.8

What is more, the **density** of the metal, very generally speaking, also *increases* with the strength of the bond. For instance, the transition metal osmium (Os) is the densest metal of the naturally occurring elements, while the alkali metal lithium (Li) is the least dense.

Another physical characteristic of metals is metallic **lustre**, which is caused by the fact that the valence electrons easily reflect incoming light, making the surface of metals shiny.

Matter that is held together by metallic bonds furthermore displays good **electrical conductivity** due to the presence of free-roaming electrons. In decreasing order of electrical conductivity, these three elements are the best conductors: silver (Ag), copper (Cu), and gold (Au). Moreover, as electrons have very little mass and move fast, they can conduct high-frequency alternating currents, unlike dissolved or molten ionic compounds whose ions are more massive and thus move slower.

Finally, the *high motility* of the valence electrons ensures that local bonds can easily be broken and recreated, so that metals can be drawn into wires, i.e., they are **ductile**, and moulded under pressure into a certain shape, i.e., they are **malleable**. In other words, metals are not brittle as is the case with ionic solids, where the electrons are fixed in position.

6.6 Inter-molecular Forces

6.6.1 The Main concept

In the previous sections, we have seen that giant network structures can be held together by ionic bonds (e.g., CaF_2), covalent bonds (e.g., SiO_2), and metallic bonds (e.g., Pb). There also exist other solids, liquids, or gases, whereby forces between their individual *covalent* molecules, called **inter-molecular forces**, are keeping these materials together. That is, the bonds *within* the molecules of which the material is made are *covalent* bonds, whereas the bonds *between* them, whose function is to hold the material together, are *weak inter-molecular* bonds.

These covalent molecules can be either simple molecular substances or macromolecular substances. The **simple molecular substances** experience weaker inter-molecular forces and are therefore usually liquids or gases. Examples include water (H_2O), ammonia (NH_3), nitrogen gas (N_2), or hydrogen chloride (HCl). In **macromolecular substances**, the weak inter-molecular forces are much stronger, so that these substances take on a solid form at room temperature. Examples include naphthalene ($C_{10}H_8$), proteins (e.g., tyrosine phosphatase $C_{72}H_{111}N_{19}O_{31}P_2$), and paraffin wax ($C_{31}H_{64}$).

6.6.2 Three Types of Inter-molecular Forces

The weak inter-molecular bonds are established between chemical substances following an asymmetry within their internal charge distribution, called a **dipole**, which leads to the formation of electrostatic forces *between* the substances. This asymmetry (dipole) arises because electrons within molecules are mobile, so that one part of a molecule could momentarily experience a slightly more negative charge (denoted as δ-) than the other side, which then displays a slightly more positive charge (indicated as δ+).

If the dipole has a *temporary* character, the inter-molecular forces are known as **London dispersion forces or van der Waals forces**, which are the *weakest* form of inter-molecular bonds. As the electrons are mobile in every molecule, it follows that *all* molecules experience London dispersion forces.

With respect to the Groups that contain *non-metallic elements*, the van der Waals forces grow stronger *down* these Groups since the additional available space in larger atoms together with a higher number of electrons translate into stronger dipoles. This translates into an increasing trend in melting and boiling points—note that this is the opposite scenario relative to alkali and alkaline earth metals (see section 6.5.2). For example, the boiling point of chlorine (Cl_2, in Period 3, Group 17) is equal to -34.6°C, whereas astatine (At_2, in Period 6, Group 17) boils at 337°C.

Keep in mind that in order for matter to change its state, for instance, from solid to liquid (i.e., melting) or from liquid to gaseous (i.e., boiling), it is the inter-molecular bonds that are being broken, *not* the intra-molecular covalent bonds (see section 15.2).

Typically, if the molecule is *non-polar*, the only type of inter-molecular forces acting between the individual non-polar substances is van der Waals forces. For example, the simple molecular compound methane (CH_4) is a non-polar compound (see Example 6.9 in section

6.4). This means that a temporary dipole in one CH_4 compound *spontaneously* induces a dipole in its neighbouring compound (e.g., the negative side of the dipole (δ-) within the first compound induces a positive charge (δ+) at the side within the second compound that is closest to the negative side of the first one), which will in turn do the same in the following compound, and so on.

With respect to *polar* compounds, not only are van der Waals forces present, but there is an additional type of inter-molecular forces acting between the compounds, called **dipole-dipole interactions**. Whereas the dipole in van der Waals forces form spontaneously in molecules, the dipole in polar compounds have a *permanent* character.

Therefore, the dipole-dipole interactions refer to the inter-molecular forces that arise as a result of the interactions between these permanent dipoles. For instance, the compound nitrogen triiodide (NI_3) is polar, so that the inter-molecular forces at play are both van der Waals forces and dipole-dipole interactions.

The additional presence of the dipole-dipole interactions *pushes up* the melting and boiling point of substances. As a case in point, even though the compounds ethane (C_2H_6) and fluoromethane (CH_3F) both contain 18 electrons, their boiling points differ, as ethane is non-polar while fluoromethane is polar. That is, ethane boils at -88.6°C, whereas the boiling point of fluoromethane lies a bit higher at -78.4°C.

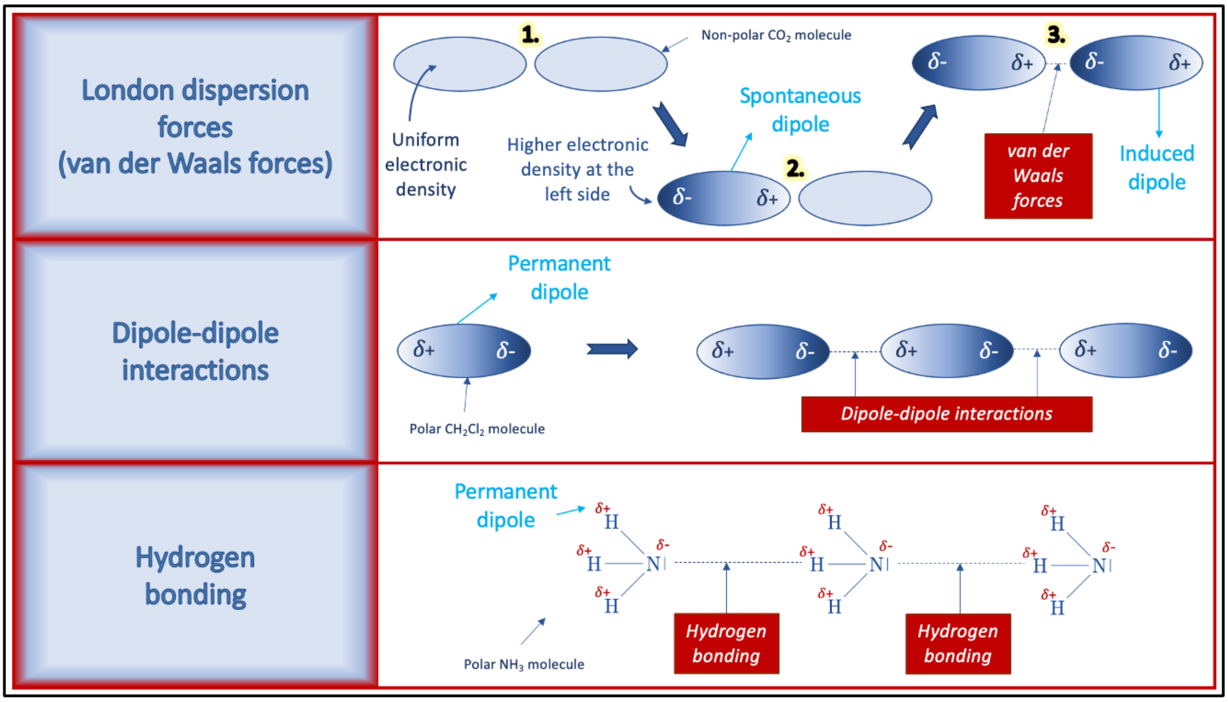


Figure 6.4: An overview of the three types of inter-molecular forces

A third type of inter-molecular forces that is discussed here is known as **hydrogen bonding**. Whenever hydrogen (H) creates a compound with the strong electronegative elements nitrogen (N), oxygen (O), or fluorine (F), an attractive force, called hydrogen bonding, emerges between the hydrogen (H) atom of one compound and the lone pair of electrons of another compound.

In the example of the polar compound hydrogen fluoride (HF), the hydrogen (H) atom of one HF compound will construct hydrogen bonds with one of the three lone pairs of electrons of the fluorine (F) atom of a next HF compound, and so on. Therefore, the inter-molecular forces that play a role in the bonding strength between HF compounds include van der Waals forces, dipole-dipole interactions as well as hydrogen bonding. The additional strength provided by hydrogen bonding explains why the boiling point of the compound HF (19.5°C) is higher compared to, for instance, the polar compound hydrogen iodide HI (-35.4°C), even if the compound (HI) is larger and has a higher number of electrons (54) relative to HF (10).

Bear furthermore in mind that although the element chlorine (Cl) is also strongly electronegative, it is a larger element with regard to the atoms N, O, and F, meaning that its electron pairs are more diffused across space and thus unsuitable to establish strong hydrogen bonds. This is why the compound hydrogen chloride (HCl) is not forming any hydrogen bonds.

In conclusion, Table 6.4 summarizes the general characteristics and the physical properties of matter in terms of the type of chemical bonding that exists between the constitutive atoms and molecules, as discussed throughout this chapter.

Table 6.4: Overview physical properties of matter in terms of bonding type

	Giant Lattice Structure			**Covalent Molecular**	
	Ionic	**Covalent**	**Metallic**	**Macro-molecular**	**Simple Molecular**
Type of substance	Compounds of metals and non-metallic elements	The element C and compounds involving Si, C, and O	Metals	Polymer	Molecules and compounds of non-metallic elements
Type of particle	Ions	Atoms	Positively charged atoms, surrounded by electron cloud	Long-chained compounds	Small molecules or compounds
Examples	MgS, KCl, or NaF	SiO_2, SiC, or diamond	Rb, Co, or Na	Proteins, $C_{15}H_{14}N_2O_5S$, or acid green	O_2, CCl_2O, or SeF_6
Type of bonds between the particles	Ionic	Covalent	Metallic	Weak inter-molecular forces	Weak inter-molecular forces
	Physical Properties			**Physical Properties**	
Hardness	Hard and brittle	Hard (except graphite)	Hard, ductile, and malleable	Soft and flexible	Soft and flexible
Electrical conductivity	High when melted or dissolved	Very poor or absent	Very high	Very poor or absent	Very poor or absent
Solubility in water	Often soluble (e.g., NaCl)	Reluctant to dissolve	Insoluble	Usually reluctant to dissolve (except for, e.g., glucose and ethanol)	Usually soluble
Melting and Boiling point	High	Very high	Usually high (very high for transition metals)	Average	Low

7 Group Chemistry

7.1 The Alkali Metals (Group 1)

7.1.1 A Definition

As indicated in Fig. 2.1, the alkali metals consist of the chemical elements of Group 1 of the Periodic Table, minus the element hydrogen ($_1$H). That is, the Group 1 metals include lithium ($_3$Li), sodium ($_{11}$Na), potassium ($_{19}$K), rubidium ($_{37}$Rb), cesium ($_{55}$Cs), and francium ($_{87}$Fr).

7.1.2 Chemical Properties

With respect to their **chemical properties**, all the alkali metals possess just one valence electron, and it resides within their s orbital—which is why these metals are part of the larger s-block (see section 2.2). As a result, their electron configuration has the general form [X] ns^1, with X being the noble gas of the Period $n-1$ and $n \geq 2$. As atoms ultimately strive for the stable octet or duplet structure of the noble gases, alkali metals have a *strong urge* to give up their single valence electron and become cations with a charge of plus one.

In chemical terms, that strong urge is translated as having low **ionization energies**, i.e., the energy needed for an atom to shed one of its valence electrons. Put another way, their **electron affinity** is weak—this is represented by high (less negative) values (see section 2.3). In fact, the alkali metals have one of the lowest ionization energies throughout the Periodic Table, which explains why they are amongst the most reactive metal elements.

What is more, when moving *down* Group 1, the **reactivity** of the alkali metals *enhances*. The underlying reason is the following. As the Period number increases, the distance from the negatively charged valence electron in the outer electron shell (the s subshell) to the atom's positively charged nucleus also increases, as the atom grows in size. This leads to a *weaker* electrostatic force between the nucleus and the electron (see section 1.1), which implies that *less energy* is required for the atom to give up its valence electron, or put differently, for another atom to steal away this atom's valence electron—this is the ionization energy.

In other words, a *lower* ionization energy—or a weaker electron affinity (less negative values)—results in *stronger* reactive behaviour by the atom of the alkali metal. Therefore, a decreasing trend in ionization energy *down* Group 1 explains why at the same time the reactivity of the alkali metals *intensifies*.

Table 7.1: The ionization energies and electron affinities of the alkali metals

Element	Period Number	Ionization Energy (in kJ·mol^{-1})	Electron Affinity (in kJ·mol^{-1})
Lithium (Li)	2	520.2	-59.6
Sodium (Na)	3	495.8	-52.8
Potassium (K)	4	418.8	-48.4
Rubidium (Rb)	5	403.0	-46.9
Cesium (Cs)	6	375.7	-45.5
Francium (Fr)	7	393.0	-46.9

Table 7.1 lists the ionization energies and electron affinities of the alkali metals and reflects this declining trend in reactivity. Note that the values for francium (Fr) are higher compared to the element one place higher up in the Group, i.e., cesium (Cs). The reason is related to effects predicted by Albert Einstein's theory of special relativity: Due to the high velocity of electrons, the distance between the orbitals and the nucleus is somewhat being contracted, leading to a stronger electrostatic force and thus a moderately higher ionization energy and slightly stronger (more negative) electron affinity.

This growing tendency in reactivity is illustrated when alkali metals come into contact with water, which is an exothermal reaction, i.e., heat is released to the immediate environment. The **general reaction between alkali metals and water** results in the production of hydrogen gas (H_2) and a compound made of the alkali metal and a hydroxide anion (OH^-). The chemical equation looks as follows (with the respective alkali metal designated by the letter A):

$$2\,\mathrm{A}(s,\,l) + 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{AOH}(aq) + \mathrm{H_2}(g) \tag{7.1}$$

In the case of lithium (Li), the reaction occurs rather slowly. From sodium (Na) and potassium (K) onwards, the produced heat is able to ignite the hydrogen gas and melt the alkali metal, and as we move down Group 1, the reactive behaviour becomes more pronounced.

As a matter of fact, this vigorous reactivity towards water *as well as oxygen* explains why the alkali metals are almost always found in a combined state, i.e., not isolated, in nature. The chemical equations for the ignition of hydrogen gas (H_2) and the metals themselves (A) are the following:

$$\begin{cases} 2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) & \longrightarrow \quad 2\,\mathrm{H_2O}(g) \\ 4\,\mathrm{A}(s,\,l) + \mathrm{O_2}(g) & \longrightarrow \quad 2\,\mathrm{A_2O}(s) \end{cases} \tag{7.2}$$

Another chemical property is known as **electronegativity**, which is defined as the tendency of an atom *within a molecule* to attract the bonding pair(s) of electrons towards itself (see also section 5.3 on oxidation states, section 6.3 on ionic bonding, and section 6.4 on covalent bonding) and is built on the notions of ionization energy and electron affinity. It is measured on the so-called Pauling scale, which runs from the lowest value of 0.7—corresponding to the alkali metal francium (Fr)—to the highest value of 3.98—corresponding to the halogen fluorine (F).

The electronegativity values of the alkali metals are among the *lowest* within the Periodic Table, which explains the presence of a diffused electron cloud in metallic bonding (see section 6.5), given that the atoms in the metal pull only weakly at the electrons so that the bonds formed do not come with directional preferences. Regarding bonds between Group 1 metals and elements that display a much higher electronegative value, such as halogens or other non-metallic elements, the bonding pair of electrons will be drawn close enough to the non-metallic atom for the electron of the alkali metal to be effectively transferred to the non-metallic element, and thereby creating an *ionic bond*.

What is more, the electronegative character of the alkali metals overall *weakens* as the Period number *increases* (see Table 7.2). The reason is that *down* Group 1, the distance between the positively charged nucleus and the bonding electrons gets *larger*, resulting in a *diminished* attractive electrostatic force and thus a *weaker* pull on the bonding pair of electrons. This in turn translates into a *stronger* ionic character of the respective bond.

Table 7.2: The electronegativity values of the alkali metals

Element	Period Number	Electronegativity Value
Lithium (Li)	2	0.98
Sodium (Na)	3	0.93
Potassium (K)	4	0.82
Rubidium (Rb)	5	0.82
Cesium (Cs)	6	0.79
Francium (Fr)	7	0.7

Let us consider the example of the ionic compounds potassium bromide (KBr) and cesium bromide (CsBr). With an atomic number of 19 and an outer electron shell configuration of $4s^1$, we know that potassium (K) harbours 19 protons and 18 *inner* electrons—these are the electrons that are not valence electrons—which gives a net attraction of +1 towards the bonding electron. For bromine (Br), the net attraction measures +7, given that its nucleus contains 35 protons and is surrounded by 28 inner electrons (as a halogen, it has an outer electron shell configuration of $4s^2\ 4p^5$). This means that the position of the bonding pair of negatively charged electrons is strongly shifted towards bromine (Br) in the compound KBr.

With respect to the element cesium (Cs) in the ionic compound CsBr, we also find a net attraction of +1 towards the bonding electrons, taking into account an atomic number of 55 and 1 valence electron. Therefore, since there is no difference in the net attraction between the two cases of KBr and CsBr, we could naively assume that the bonding pair of electrons would in both cases be located at the same distance from the bromine (Br) atom.

However, as the potassium (K) atom is *smaller* than the cesium (Cs) atom, the bonding electrons in the compound KBr experience a slightly *stronger* pull by the potassium (K)'s net attraction of +1 (relative to the net attraction of +1 of the cesium (Cs) atom in CsBr) and thus are positioned a bit closer to the potassium (K) atom (relative to the position of the bonding electrons with respect to the cesium (Cs) atom in CsBr). The *stronger* ionic character of the CsBr compound is also reflected by a *greater* difference in electronegativity (ΔEN; see also section 6.4). That is, for the KBr compound, we find a difference of $\Delta\text{EN} = 2.14$, whereas for the CsBr compound the value is slightly higher, i.e., $\Delta\text{EN} = 2.17$.

7.1.3 Physical Properties

When it comes to the **physical properties** of the alkali metals, the **size of the atom** expands down Group 1, since with every incremental step in the Period number n an additional electron shell is added to the atom. What is more, as the mass number A of the elements increases down the Group, their **atomic mass** grows larger as well. In addition, the **density** generally follows the same trend, except for potassium (K), as its expansion in size outweighs the gain in mass. The alkali metals are among the least dense elements within the Periodic Table.

Table 7.3 summarizes various physical properties of the Group 1 elements. Note that the atomic radius is given in picometer (pm), which is equal to 10^{-12} m.

Table 7.3: Some of the physical properties of the alkali metals

Element	Atomic Number Z	Atomic Mass (in amu)	Atomic Radius (in pm)	Density (in g·cm^{-3})	Melting Point (in °C)	Boiling Point (in °C)
Lithium (Li)	3	6.94	152	0.534	180.5	1,347
Sodium (Na)	11	22.99	186	0.971	97.8	882.9
Potassium (K)	19	39.10	227	0.862	63.25	760
Rubidium (Rb)	37	85.47	248	1.532	39.31	688
Cesium (Cs)	55	132.91	265	1.873	28.4	669
Francium (Fr)	87	223	270	/	26.8	677

Alkali metals are typically **soft** and **lustrous**, find themselves in a **solid** state at room temperature and pressure (except for the element francium (Fr), which may be rather liquid, given a melting point of 26.8°C), and display a **silvery-white** colour (cesium (Cs) is more silvery-gold coloured). As solid metals, they furthermore make excellent **electrical and thermal conductors** due to the presence of free electrons (see section 6.5).

As already alluded to in section 6.5, an increasingly debilitating electrostatic force down the Group (as a result of a growing atomic radius) is responsible for weaker bonds between the nuclei and the electron cloud, which in turn explains the declining trend in the **melting and boiling points** of the alkali metals. Bear in mind that the boiling point on average is much higher than the melting point, given that much more energy is required to *completely severe* the ties between the compounds (which signals the gas phase), instead of only *moderately weakening* the ties (which marks a liquid state).

7.2 The Halogens (Group 17)

7.2.1 A Definition

Within the p-block of the Periodic Table (see Fig. 2.1), we encounter the elements fluorine ($_{9}$F), chlorine ($_{17}$Cl), bromine ($_{35}$Br), iodine ($_{53}$I), astatine ($_{85}$At), and tennessine ($_{117}$Ts) in Group 17, which are collectively known as the **halogens**.

7.2.2 Chemical Properties

Regarding their **chemical properties**, the halogens display an **outer electron configuration** of the form $ns^2\ np^5$, with n the respective Period number, which implies that they all harbour seven valence electrons. In other words, they have a strong tendency to form anions (e.g., Br$^-$), called **halide ions**, in order to obtain the *stable octet structure* of the noble gas that is located one position to the right of the respective halogen in the Periodic Table, i.e., the noble gas that belongs to the same Period as the halogen (in the case of bromine (Br), the respective noble gas is krypton (Kr)).

Put another way, the halogens exhibit the highest **electron affinities** (i.e., the most negative values) in the Periodic Table. Not only that, their specific electronic configuration is the reason why they all form non-polar covalent diatomic molecules (e.g., Cl_2 or At_2), which possess a very strong **oxidizing ability**.

Because of this strongly pronounced urge to attract an electron, which is reflected by their strong electron affinity, the halogens are not only among the most reactive non-metallic elements—they are especially reactive when forming bonds with the alkali metals (as well as the alkaline earth metals of Group 2)—but they also exhibit one of the highest values of **ionization energies** throughout the Periodic Table. Put differently, since halogens only need one additional electron to achieve the octet configuration, it takes a large amount of energy to *remove* an electron from their outer electron shell.

As a matter of fact, electron affinity and ionization energy are *inversely related* to one another. That is, halogens are associated with *lower* (more negative) values of electron affinity—which means a strong affinity for electrons—and *higher* ionization energies, whereas alkali metals display *higher* (less negative) values of electron affinity—which means a weak affinity for electrons—and *lower* ionization energies.

When it comes to the property of **electronegativity**, halogens have a *strong* electronegative character, with fluorine (F) possessing the highest value (i.e., 3.98) in the Periodic Table.

What is more, as one moves *down* Group 17, both electronegativity, electron affinity, and ionization energy follow the same trend as the one observed in the case of alkali metals: the values of electronegativity and ionization energy *decrease*, while those of electron affinity *increase*. An exception in this trend is the electron affinity of fluorine (F) due to the strong repulsion between its valence electrons (it is a small atom), so that a new electron will experience a slightly weaker electrostatic force from its nucleus, which results in a lower electron affinity, i.e., a less negative value, compared to chlorine (Cl).

Table 7.4: The electronegativity, ionization energy, and electron affinity of the halogens

Element	Period Number	Atomic Number Z	Electro-negativity Value	Ionization Energy (in kJ·mol^{-1})	Electron Affinity (in kJ·mol^{-1})
Fluorine (F)	2	9	3.98	1,681	-328.2
Chlorine (Cl)	3	17	3.16	1,251	-348.6
Bromine (Br)	4	35	2.96	1,140	-324.5
Iodine (I)	5	53	2.66	1,008	-295.2
Astatine (At)	6	85	2.2	917	-233.1
Tennessine (Ts)	7	117	/	743	-165.9

However, unlike the alkali metals, the **reactivity** of the halogens *declines* down the Group—in other words, the *ionic character* of the halogens becomes less explicit—because it becomes increasingly difficult to attract an electron due to a growing atomic radius, which in turn implies a weaker electrostatic force between the bonding electrons and the atom's nucleus. Their high reactivity furthermore implies that halogens are toxic, with their toxicity diminishing down the Group.

One of the consequences of this declining trend in reactivity is the fact that *more* reactive halogens can displace *less* reactive ones from their aqueous salty solutions. These chemical reactions are called **halogen displacement reactions**, and the reaction mixture obtains a darker colour, since the halogens display a darker colour *down* the Group (see their physical properties further below). Note that a salt is defined as an ionic compound involving a metal cation and a non-metallic anion, such as a halide ion, and is the result of the reaction between a base and an acid, i.e., a neutralization reaction (see section 3.3 and section 9.3).

For example, when a solution of chlorine (Cl_2), which has a yellow-green colour, reacts with the colourless ionic compound sodium bromide (NaBr), a reddish-brown coloured mixture is created, because chlorine (Cl) has replaced bromine (Br) within the salty solution NaBr—chlorine (Cl) is more reactive than bromine (Br)—to form the colourless NaCl solution and the bromine (Br) solution, which has a reddish-brown colour. The chemical equation looks as follows:

$$\underset{\text{(yellow-green)}}{\mathrm{Cl_2}(aq)} + \underset{\text{(colourless)}}{2\,\mathrm{NaBr}(aq)} \longrightarrow \underset{\text{(colourless)}}{2\,\mathrm{NaCl}(aq)} + \underset{\text{(reddish-brown)}}{\mathrm{Br_2}(aq)} \tag{7.3}$$

Equation 7.3 reveals that *halogens are converted into halide ions, and vice versa.* As a matter of fact, this is precisely the definition of a **redox reaction** (see section 5), which takes the following form:

$$\begin{cases} \text{Oxidation:} & 2\,\mathrm{Br}^-(aq) \longrightarrow \mathrm{Br_2}(aq) + 2\,\mathrm{e}^- \\ \text{Reduction:} & \mathrm{Cl_2}(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Cl}^-(aq) \end{cases} \tag{7.4}$$

Another example examines the reaction between bromine (Br_2) with potassium iodide (KI) which produces a darker brown mixture of iodine (I_2) and potassium bromide (KBr), as bromine (Br) is more reactive than iodine (I). The chemical and redox reactions are written as follows:

$$\begin{gathered} \underset{\text{(reddish-brown)}}{\mathrm{Br_2}(aq)} + \underset{\text{(colourless)}}{2\,\mathrm{KI}(aq)} \longrightarrow \underset{\text{(colourless)}}{2\,\mathrm{KBr}(aq)} + \underset{\text{(dark brown)}}{\mathrm{I_2}(aq)} \\ \begin{cases} \text{Oxidation:} & 2\,\mathrm{I}^-(aq) \longrightarrow \mathrm{I_2}(aq) + 2\,\mathrm{e}^- \\ \text{Reduction:} & \mathrm{Br_2}(aq) + 2\,\mathrm{e}^- \longrightarrow 2\,\mathrm{Br}^-(aq) \end{cases} \end{gathered} \tag{7.5}$$

Redox reactions 7.4 and 7.5 show that chlorine (Cl_2) and bromine (Br_2), respectively, are **oxidizing agents**. In fact, the halogens' oxidizing ability *reduces* in strength *down* Group 17. Table 7.5 provides an overview of the possible halogen displacement reactions when considering the elements chlorine (Cl), bromine (Br), and iodine (I). Bear in mind that due to the very strong oxidizing ability of fluorine (F), it oxidizes water into oxygen, making fluorine (F) typically unfit for solution reactions.

Table 7.5: Overview of the halogen displacement reactions for halogens

		Halides		
		NaCl	**NaBr**	**Nal**
Halogens	**Cl_2**	No reaction	• Products: NaCl, Br_2 • Colour mixture: reddish-brown	• Products: NaCl, I_2 • Colour mixture: dark brown
	Br_2	No reaction	No reaction	• Products: NaBr, I_2 • Colour mixture: dark brown
	I_2	No reaction	No reaction	No reaction

7.2.3 Physical Properties

When it comes to their **physical properties**, besides an expanding **size**, **mass**, and **density** down the Group, also the **melting and boiling points** of the halogens *increase* due to the growing van der Waals forces—this is the *opposite* trend with respect to the alkali metals. Remember that an expanding atomic size and a higher number of electrons are the reason why these London dispersion forces become more prominent down the Group (see section 6.6).

As a result, fluorine (F) and chlorine (Cl) come in **gaseous** form (with a pale yellow and yellow-green colour, respectively), bromine (Br) takes on a **liquid** state (with reddish-brown colour), and iodine (I), astatine (At), and Tennessine (Ts) are **solids** (with a blue-black, dark pink-blackish, and black colour, respectively), at the standard temperature and pressure conditions.

In addition, halogens are *poor* **electrical and thermal conductors**, since there are no free electrons available—as in the case with alkali metals—given their great reluctance to lose electrons (high ionization energies) and great ease to attract them (strong electron affinity, which is represented by more negative values).

Table 7.6: Some of the physical properties of the halogens

Element	**Atomic Mass (in amu)**	**Ionic Radius (in pm)**	**Density (in g·cm^{-3})**	**Melting Point (in °C)**	**Boiling Point (in °C)**	**Physical State (at STP)**
Fluorine (F)	19.00	133	1.696	-219.6	-188.1	gas
Chlorine (Cl)	35.45	181	3.214	-101.6	-34.0	gas
Bromine (Br)	79.90	196	3.103	-7.3	58.8	liquid
Iodine (I)	126.90	220	4.933	113.7	184.3	solid
Astatine (At)	210	/	6.4	302	337	solid
Tennessine (Ts)	294	/	7.2	/	/	solid

When discussing the halogens, astatine (At) and tennessine (Ts) are usually left out of the discussions because they are unstable, radioactive elements. Astatine (At) decays into other elements and products within less than a minute, and only a total amount of less than 1 g is present in the entire Earth's crust. Tennessine (Ts) does not even occur naturally, as it is a synthetic element. The other four halogens are found in nature in the form of halides within salts. Specifically, the halides are present in minerals (e.g., cryolite (Na_3AlF_6)), rock salt (e.g., NaCl), salty lakes, and oceans.

7.3 The Noble Gases (Group 18)

7.3.1 A Definition

The final column of the Periodic Table contains the **noble or inert gases**, i.e., helium ($_2$He), neon ($_{10}$Ne), argon ($_{18}$Ar), krypton ($_{36}$Kr), xenon ($_{54}$Xe), radon ($_{86}$Rn), and oganesson ($_{118}$Og).

7.3.2 Chemical Properties

Concerning their **chemical properties**, the outer electron shell of the noble gases has attained the most energetically favourable situation, which is known as the **octet configuration** or, in the case of helium (He), the **duplet configuration**. As a result, their valence shell takes on the form of $ns^2\ np^6$ and $1s^2$, respectively, with n the Period number and $n \geq 2$.

In other words, noble gases are extremely resistant to either lose a valence electron, which results in high **ionization energies**, or gain an additional electron, which translates into a very low **electron affinity**—all the noble gases display positive values of electron affinity, meaning that it requires energy to adopt a new valence electron. Therefore, due to their fully filled valence electron shells, the amount of **reactivity** of the noble gases is the lowest among all the elements within the Periodic Table, which is why they usually do not form any compounds.

One of the consequences of their inactivity is that they typically do not react with oxygen (O) in the air, which qualifies them as non-flammable gases.

Table 7.7: The electronegativity, ionization energy, and electron affinity of the noble gases

Element	**Period Number**	**Atomic Number Z**	**Electro-negativity Value**	**Ionization Energy (in kJ·mol^{-1})**	**Electron Affinity (in kJ·mol^{-1})**
Helium (He)	1	2	/	2,372	0
Neon (Ne)	2	10	/	2,081	29
Argon (Ar)	3	18	/	1,521	35
Krypton (Kr)	4	36	3.0	1,351	39
Xenon (Xe)	5	54	2.6	1,170	41
Radon (Rn)	6	86	/	1,037	41
Oganesson (Og)	7	118	/	/	/

Notwithstanding their inactivity, some of the heavier noble gases, such as krypton (Kr), xenon (Xe), and radon (Rn), can in fact under certain circumstances engage in compound formation with the elements oxygen (O) and fluorine (F) as a result of the very high **electronegativity** values of both oxygen (O) and fluorine (F), i.e., 3.44 and 3.98, respectively, and of an increasing instability of the noble gases down the Group (due to a growing radius and a declining ionization energy).

Some examples include the thermally unstable krypton difluoride (KrF_2), the stable compounds xenon difluoride (XeF_2), xenon tetrafluoride (XeF_4), and xenon hexafluoride (XeF_6) as well as the stable liquid xenon oxytetrafluoride ($XeOF_4$), the radioactive radon difluoride (RnF_2), and the explosive compounds xenon tetroxide (XeO_4) and xenon trioxide (XeO_3). Other stable compounds are manufactured as a result of applying high amounts of pressure, e.g., the compounds argon difluoride (ArF_2) and disodium helide (Na_2He).

One example of a chemical reaction with noble gases includes the reaction of xenon hexafluoride (XeF_6) with water (H_2O) to form an aqueous solution of xenon trioxide (XeO_3)—which is not explosive unlike the dry and solid form of XeO_3—and hydrofluoric acid (HF):

$$\mathrm{XeF_6}(s) + 3\,\mathrm{H_2O}(l) \longrightarrow \mathrm{XeO_3}(aq) + 6\,\mathrm{HF}(aq) \tag{7.6}$$

7.3.3 Physical Properties

With respect to their **physical properties**, the noble gases at room temperature and pressure are monatomic, colourless, odourless *gases*, except oganesson (Og), which is likely a *liquid* at these conditions. Moreover, *down* Group 18, the noble gases *gain* in **size**, **mass**, and **density**, a trend similar to the alkali metals and halogens.

Noble gases are furthermore very good **insulators**—as in the case of halogens—but become electrically conductive at low pressure.

Regarding their **melting and boiling points**, they are amongst the *lowest* within the Periodic Table—the element Helium (He) has the lowest melting and boiling point of all the chemical elements—because only weak van der Waals forces are present to hold the atoms together and thus relatively little energy is required to overcome them. What is more, the melting and boiling points *increase* down the Group, since the van der Waals forces grow stronger (see section 6.6).

Table 7.8: Some of the physical properties of the noble gases

Element	**Atomic Mass (in amu)**	**van der Waals Radius (in pm)**	**Density (in g·dm^{-3})**	**Melting Point (in °C)**	**Boiling Point (in °C)**
Helium (He)	4.00	140	0.179	-272.2	-268.9
Neon (Ne)	20.18	154	0.900	-248.5	-246.1
Argon (Ar)	39.95	188	1.782	-189.6	-185.9
Krypton (Kr)	83.80	202	3.708	-157.4	-152.3
Xenon (Xe)	131.29	216	5.851	-111.5	-107.1
Radon (Rn)	222.0	220	9.97	-71.2	-61.7
Oganesson (Og)	294	/	/	/	76.8

8 Separation Techniques

8.1 Mixtures and Compounds

As briefly touched upon in section 6.1, it requires **chemical reactions** to take apart molecules into their individual elements, whereas the substances within mixtures can be separated with the help of **physical processes**. Examples of molecules are water (H_2O), iodine (I_2), and sodium fluoride (NaF), while examples of mixtures include seawater, air, and blood.

With regard to liquid mixtures, a distinction can be made between miscible and immiscible liquids. In the case of **miscible liquids**, two or more liquids that are joined together will form a *homogeneous* solution, since they possess *similar* intermolecular interactions due to a similar polarity.

For example, the mixture gasoline contains, among other substances, the miscible liquids heptane (C_7H_{16}) and octane (C_8H_{18})—they are miscible as they are both non-polar compounds and experience both van der Waals forces. Another example is the mixture of methanol (CH_3OH) and water (H_2O). Given that both are polar substances and form hydrogen bonds, they display similar intermolecular interactions, so that methanol is miscible with water.

However, when the polarity differs among the liquids, the mixture is *heterogenous*, i.e., the liquids will not mix and they are referred to as **immiscible liquids**. Take the example of ethylbenzene ($C_6H_5CH_2CH_3$), which is used in paints and synthetic rubber, and water (H_2O). The non-polarity of ethylbenzene and the polarity of water results in different intermolecular interactions, so that they are immiscible, i.e., they do not mix.

When considering mixtures of solids and liquids, a distinction can be drawn between **dissolved solids**, which form *homogeneous* mixtures, and **insoluble solids**, which result in *heterogeneous* mixtures. For instance, mixing silver chloride (AgCl) with water (H_2O) leads to a heterogeneous mixture, as AgCl is insoluble in water—the energy to hydrate the ions Ag^+ and Cl^- to form AgOH and HCl is not sufficient to overcome the forces that bind the atoms in the lattice structure of AgCl. In contrast, the solid silver chloride (AgCl) dissolves in an aqueous solution of ammonia (NH_3), as it forms the cation $[Ag(NH_3)_2]^+$.

Another way to distinguish between mixtures and compounds is the knowledge that the **composition** of elements within a compound always remains *constant*, while that of a mixtures *does not*. For instance, the compound potassium sulfide (K_2S) will always contain 29% sulphur (S) and 71% potassium (K) in terms of atomic mass, but seawater can have different amounts of salt in it.

In addition, it is useful to look in a bit more detail at the difference between physical and chemical changes. A **physical change** is the process whereby the individual substances do not transform into other substances. These changes are usually accompanied by a *phase change*, such as melting, freezing, condensation, or evaporation (see section 15.2).

A **chemical change**, on the other hand, involves the rearrangement of the individual elements of the original substances and thereby forming new substances (see section 3.1). During a chemical change, the total mass of the reactants must equal the total mass of the products under ideal conditions, since no atoms can be created or destroyed during the process (see section 3.3). Examples of chemical changes include combustion, rotting, iron rusting, and food metabolism.

Table 8.1 provides an overview of some of the characteristic dissimilarities between physical and chemical changes.

Table 8.1: Physical versus chemical changes

Criteria	Physical change	Chemical change
Substance	Substances do not transform	The reactants are recombined into new substances called products
Reversibility	Usually involves a reversible process	Typically irreversible
Change in energy	Little or none	Either exothermic (produces energy) or endothermic (requires energy)
Change in colour	No	May happen
Phase change	Usually yes	Not necessarily

8.2 Physical Separation Techniques

There are a number of physical processes that can be applied to separate the different substances within mixtures. In this section, we briefly examine the following separation techniques: simple and fractional distillation, the use of a separating funnel, evaporation, crystallization, filtration, centrifugation, and paper chromatography.

In the case of **two miscible liquids whose boiling points differ significantly from one another ($\geq$ 30°C)**, the method of **simple distillation** can be used to separate the two liquids. The process occurs roughly as follows. A mixed solution is gradually being heated in a distilling flask. When the temperature reaches the boiling point of the most volatile liquid, i.e., the liquid with the lowest boiling point, this substance transforms from a liquid into a gaseous state, leaving behind the less volatile substance still in its liquid form. The generated vapour is then guided through a water condenser, converting the vapour back into a liquid, which is eventually collected in a receiving flask. An example is the simple distillation of acetone (C_3H_6O), which boils at 56°C, and pure water (H_2O), whose boiling point is 100°C. In other words, it is the vapour of acetone that is being gathered first.

Simple distillation is also useful when a soluble solute, i.e., a **dissolved solid**, (or a non-volatile dissolved impurity) must be separated from a homogeneous solution, whereby the vapourized solvent is *stored* instead of being lost to the environment (as in the case of evaporation and crystallization). An example is the simple distillation of salty water, whereby the water vapour is gathered when the solution boils. The remaining solid residue in the distilling flask then consists of salt (NaCl), as it has a much higher boiling point (1,413°C) than water. This procedure is also a way to establish the *purity* of a watery solution: The higher its boiling point above 100°C, the greater the amount of impurities in the water.

If the mixture is an ensemble of **two or more miscible liquids with individual boiling points less than 30°C apart from one another**, a more accurate way to separate the liquids is called **fractional distillation**. The difference with simple distillation is that in fractional distillation the vapour first passes through a *fractionating column* before entering the condenser. The fractional column is a tube that contains several glass beads or ceramic plates where multiple simple distillations take place, so that the percent composition of the *most volatile* substance increases with the height of the column. For instance, fractional distillation can be applied to separate methanol (CH_3OH), with a boiling point of 64.7°C, from ethanol (CH_3CH_2OH), which boils at 78.2°C.

A next technique makes use of a **separating funnel**, which can be employed to physically separate **two immiscible liquids**. The mixture is poured into the funnel, and after some time, the liquid with the higher density forms the bottom layer, on top of which the liquid with the lower density rests. At the bottom of the funnel, a tap can be opened, letting the high-density liquid run out of the funnel into a collecting device. For example, the non-polar compound pentane (C_5H_{12}) and the polar compound acetic acid (CH_3COOH) are immiscible liquids, whereby acetic acid will form the bottom layer due to a higher density ($1.049\ \text{g}\cdot\text{ml}^{-1}$) relative to that of pentane ($0.626\ \text{g}\cdot\text{ml}^{-1}$).

Regarding a mixture of a **dissolved solid** (i.e., a soluble solute) within a solution, two similar separation processes can be of assistance: evaporation and crystallization. With respect to **evaporation**, the solution is simply being heated for the time necessary for *all the water* to boil off. What remains is the solid solute, so that the dissolved solid has effectively been separated from the solvent. Examples of soluble solids in water include sodium carbonate (Na_2CO_3), copper(II) sulfate ($CuSO_4$), and magnesium chromate ($MgCrO_4$).

In contrast, the technique of **crystallization** does not allow the evaporation of *all* the water present. Rather, the solution is heated and evaporated until it forms a *saturated solution*—this is a solution whereby the maximum amount of solute is dissolved within the solvent (see section 4.4.2)—whereupon crystals form when cooled, which are then left to dry. For instance, crystals of glucose ($C_6H_{12}O_6$) can be created through this procedure (note that crystallization is preferred to evaporation, since glucose could decompose under full evaporation).

Concerning the separation of **insoluble solids** from a solution, two mechanical methods can be applied. A first technique called **filtration** consists of pouring a mixture through a filtering medium, whereby the insoluble particles become entangled with this medium, so that we end up with the original pure solvent. Examples include sand, microplastics, or chalk mixed in water.

However, if the particles are too small for the filtering medium, another technique, i.e., **centrifugation**, can be used instead. A centrifuge tube containing the mixture is inserted into a rotor, which is then being spun at high rotation speeds. Due to a higher density of the solid particles combined with the force of gravity, the particles are rotated towards the bottom of the tube, whereas the lower-density substances of the solvent remain higher up in the tube. For instance, from a blood sample, centrifugation is able to separate various components, including plasma, which forms the upper layer in the centrifuge tube, lymphocytes, which settle right under the plasma, and red blood cells, which accumulate at the bottom of the tube.

A final separation technique of mixtures that is discussed in this section is referred to as **paper chromatography**, which aims to **identify the different compounds present in a liquid**. This method is often applied when a mixture is made of a number of different coloured substances, such as dyes, inks, and colouring agents in food. But it can equally be used to separate drugs from the bloodstream.

How paper chromatography works, is as follows. Droplets of the mixture are placed onto a straight line, i.e., the base line, which is drawn with a pencil on a piece of paper. As the paper is lowered into a solvent, the solvent pervades the paper and travels towards the top of the little piece of paper. During this upwards motion, the mixture dots become spread out towards the top of the paper, as the different substances move upwards along with the solvent. The identification of the various substances is then manifested due to the *different speeds* at which the substances travel, so that a layered pattern appears.

The *retardation factor* R_f expresses the extent of solubility of a particular substance and is defined as follows:

$$R_f = \frac{Distance\ traveled\ by\ the\ substance}{Distance\ traveled\ by\ the\ solvent} \tag{8.1}$$

whereby the distances are measured from the base line (i.e., the pencil line) and R_f lies in the range between 0 and 1. In other words, the *higher up* an individual substance travels on the paper, the *more soluble* it is within that specific solvent, which is in turn represented by a *higher* retardation factor R_f.

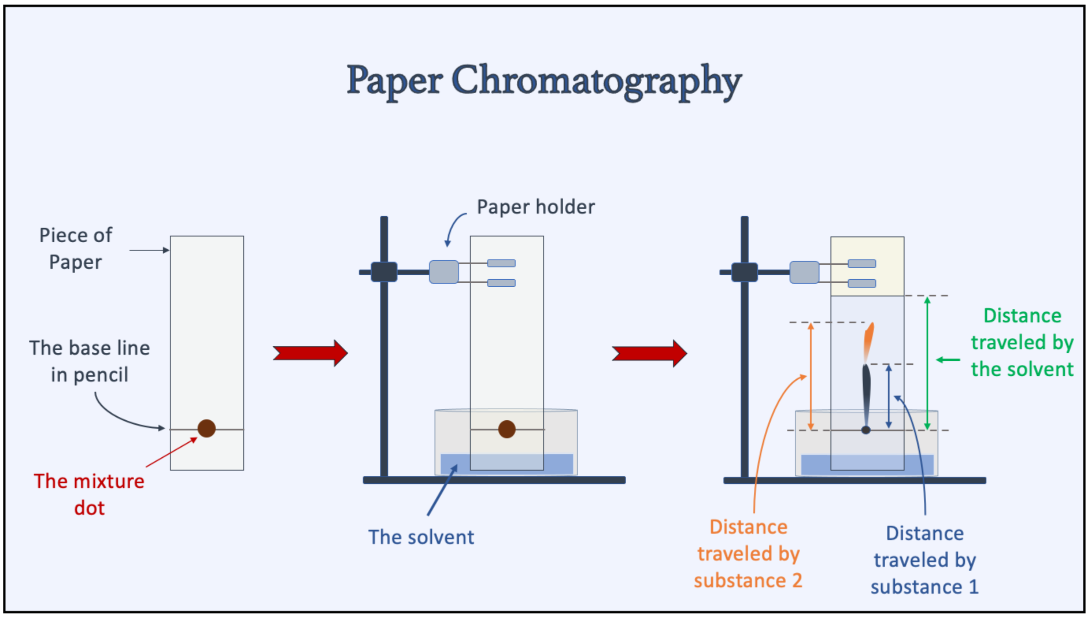


Figure 8.1: The technique of paper chromatography

Paper chromatography is furthermore a useful tool to establish the *purity* of a substance, which is determined as follows: A *pure* substance is represented by the presence of *only one* blob on the piece of paper, whereas an *impure* substance will reveal *more than one* blob.

9 Acids, Bases, and Salts

9.1 Acids

An **acid** can be defined either as a substance that ionizes in an aqueous solution and delivers hydrogen ions (H^+)—this is the Arrhenius definition—or as a substance that is a proton (H^+) *donor*—this is the Brønsted-Lowry definition, which is more general than the Arrhenius definition.

Moreover, an acid that completely dissociates in ions in an aqueous solution is referred to as a **strong acid**, whereas an acid that partially dissolves is designated as a **weak acid**. Examples of a strong acid include hydrochloric acid (HCl), hydroiodic acid (HI), nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrobromic acid (HBr), and perchloric acid ($HClO_4$), while some weak acids are hydrofluoric acid (HF), carbonic acid (H_2CO_3), hydrosulphuric acid (H_2S), phosphoric acid (H_3PO_4), acetic acid (CH_3COOH), and ammonium (NH_4^+). The respective chemical reactions of dissociation in an aqueous solution can be formulated as follows:

$$
\begin{aligned}
&\textit{Strong acids} \quad \begin{cases}
\mathrm{HCl}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{Cl}^-(aq) \\
\mathrm{Hl}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{l}^-(aq) \\
\mathrm{HNO_3}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{NO_3^-}(aq) \\
\mathrm{H_2SO_4}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{HSO_4^-}(aq) \\
\mathrm{HBr}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{Br}^-(aq) \\
\mathrm{HClO_4}(aq) & \longrightarrow \quad \mathrm{H}^+(aq) + \mathrm{ClO_4^-}(aq)
\end{cases} \\
&\textit{Weak acids} \quad \begin{cases}
\mathrm{HF}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{F}^-(aq) \\
\mathrm{H_2CO_3}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{HCO_3^-}(aq) \\
\mathrm{H_2S}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{HS}^-(aq) \\
\mathrm{H_3PO_4}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{H_2PO_4^-}(aq) \\
\mathrm{CH_3COOH}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{CH_3COO}^-(aq) \\
\mathrm{NH_4^+}(aq) & \rightleftharpoons \quad \mathrm{H}^+(aq) + \mathrm{NH_3}(aq)
\end{cases}
\end{aligned}
\tag{9.1}
$$

Another distinction can be made between dilute and concentrated acids, whereby the relative amount of aqueous solution in the mixture—or, alternatively, the relative amount of acid—is the distinguishing characteristic. That is, a **dilute acid** contains, for instance, 80% or 90% water, whereas a **concentrated acid** possesses a larger amount of acid in the mixture with respect to the solution. For example, 96% sulphuric acid (H_2SO_4) is a concentrated acid, while 6% phosphoric acid (H_3PO_4) is a dilute acid. However, there are exceptions to this convention. As a counterexample, the maximum amount of hydrogen chloride gas (HCl) that can be dissolved in water is approximately 37%, so that, for instance, 35% HCl represents a concentrated acid.

Acidic solutions can be fashioned from the **reaction between non-metal oxides and water**. Examples of non-metal oxides include sulphur dioxide (SO_2), sulphur trioxide (SO_3), carbon dioxide (CO_2), nitric oxide (NO), nitrogen pentoxide (N_2O_5), diphosphorus trioxide (P_2O_3), and phosphorus pentoxide (P_2O_5). A couple of examples of reactions are the following:

$$\left\{\begin{array}{lclcll} P_4O_{10}(s) & + & 6\,H_2O(l) & \longrightarrow & 4\,H_3PO_4(aq) & (\textit{Phosphoric acid}) \\ N_2O_5(g) & + & H_2O(l) & \longrightarrow & 2\,HNO_3(aq) & (\textit{Nitric acid}) \\ P_2O_3(s) & + & 3\,H_2O(l) & \longrightarrow & 2\,H_3PO_3(aq) & (\textit{Phosphorous acid}) \end{array}\right. \tag{9.2}$$

In the context of the formation of **acid rain** (see section 17.3), the non-metal oxides sulphur dioxide (SO_2), carbon dioxide (CO_2), and nitric oxide (NO) react with oxygen (O_2) and water (H_2O) to produce acidic solutions. The sources of these non-metal oxides can be either man-made or natural. For instance, carbon dioxide (CO_2) originates from both natural decomposition and fossil-fuel combustion, sulphur dioxide (SO_2) from volcanic gases and the burning of fossil fuels, and nitric oxide (NO) from lightning and internal combustion by vehicles. The respective chemical equations have the following form:

$$\begin{array}{ll} \textit{Carbonic acid} & \left\{\begin{array}{lclclcl} CO_2(g) & + & H_2O(l) & \longrightarrow & H_2CO_3(aq) & & \\ H_2CO_3(aq) & & & \rightleftharpoons & H^+(aq) & + & HCO_3^-(aq) \end{array}\right. \\ & \\ \textit{Sulphuric acid} & \left\{\begin{array}{lclclcl} 2\,SO_2(g) & + & O_2(g) & \longrightarrow & 2\,SO_3(g) & & \\ SO_3(g) & + & H_2O(l) & \longrightarrow & H_2SO_4(aq) & & \\ H_2SO_4(aq) & & & \longrightarrow & H^+(aq) & + & HSO_4^-(aq) \end{array}\right. \\ & \\ \textit{Nitric acid} & \left\{\begin{array}{lclclcl} 2\,NO(g) & + & O_2(g) & \longrightarrow & 2\,NO_2(g) & & \\ 3\,NO_2(g) & + & H_2O(l) & \longrightarrow & 2\,HNO_3(aq) & + & NO(g) \\ HNO_3(aq) & & & \longrightarrow & H^+(aq) & + & NO_3^-(aq) \end{array}\right. \end{array} \tag{9.3}$$

What is more, acids can be categorized according to the number of protons (H^+) that they are able to donate. If an acid donates only one hydrogen cation, it is called a **monoprotic acid**. Hydrochloric acid (HCl), benzoic acid ($C_6H_5CO_2H$), and acetic acid (CH_3COOH) are examples of monoprotic acids. As soon as an acid is capable of donating more than one proton, it is referred to as a **polyprotic acid**. Sulphuric acid (H_2SO_4), chromic acid (H_2CrO_4), and oxalic acid ($H_2C_2O_4$) are **diprotic acids**, since they are able to give away *two* protons, whereas citric acid ($C_6H_8O_7$) and phosphoric acid (H_3PO_4) are known as **triprotic acids**, as they possess the capacity of donating *three* protons.

In the case of polyprotic acids, this means that one mole of an acidic substance is able to donate *more than* one mole of protons. For instance, one mole of carbonic acid (H_2CO_3) can produce two moles of protons, while one mole of phosphorus acid (H_3PO_4) is able to generate three moles of protons:

$$\left\{\begin{array}{lcl} H_2CO_3(aq) & \rightleftharpoons & 2\,H^+(aq) + CO_3^{2-}(aq) \\ H_3PO_4(aq) & \rightleftharpoons & 3\,H^+(aq) + PO_4^{3-}(aq) \end{array}\right. \tag{9.4}$$

Another way to characterize an acid is by considering the amount of concentration of hydrogen cations (H^+), which is captured by the concept of **pH value**—pH stands for *pondus* *hydrogenii* or the potential of hydrogen—and is defined as follows:

$$pH = -\log\left([\mathrm{H}^+]\right) \tag{9.5}$$

with $[\mathrm{H}^+]$ indicating the concentration of protons and log the logarithm of base 10 ($\log_{10}$). That is, for every tenfold *increase* of the concentration of hydrogen ions, the pH value *decreases* by one unit. The pH value ranges from 0 to 14; a substance with a *pH value of 7* is regarded as a *neutral* substance, while a substance is taken to be **acidic if pH<7**.

For example, let us calculate the pH value of a 1 L solution that contains 0.8 g sulphuric acid (H_2SO_4). In a first step, we determine the number of moles that is equivalent to this mass. Based on Equation 4.2, we find that $n_{(\mathrm{H_2SO_4})} = 8.16 \times 10^{-3}$ mol (with $M_r(\mathrm{H_2SO_4}) = 98.09$ g$\cdot mol^{-1}$). Given that there are two hydrogen atoms—and thus two protons—for every H_2SO_4 compound, it follows that $n_{(\mathrm{H}^+)} = 2 \times (8.16 \times 10^{-3})$ mol $= 1.63 \times 10^{-2}$ mol. This means that the molarity or concentration of protons per liter solution (as per Equation 4.8) is expressed as $c_{(\mathrm{H}^+)} = [\mathrm{H}^+] = \frac{1.63 \times 10^{-2}}{1}\ mol \cdot L^{-1} = 1.63 \times 10^{-2}\ mol \cdot L^{-1}$. This gives a pH value of $pH = -\log(1.63 \times 10^{-2}) = -(\log(1.63) + \log(10^{-2})) = -(0.21 - 2) = 1.79$, indicating that the solution is acidic ($1.79 < 7$).

9.2 Bases

Similar to the definition of an acid, a **base** can be described as a substance that either produces hydroxide ions (OH^-) in aqueous solutions—this is according to the Arrhenius definition—or is defined as a proton (H^+) *acceptor*—in the context of the broader Brønsted-Lowry definition.

Also in the case of bases, a distinction can be made between weak and strong bases, which follow the same definition as acids. That is, a **strong base** dissolves entirely in an aqueous solution, while a **weak base** only dissociates to a certain extent. The **eight strong bases**, which are all soluble solids, are lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), rubidium hydroxide (RbOH), cesium hydroxide (CsOH), calcium hydroxide ($\mathrm{Ca(OH)_2}$), strontium hydroxide ($\mathrm{Sr(OH)_2}$), and barium hydroxide ($\mathrm{Ba(OH)_2}$).

The generalized chemical equations for the dissociation reaction of the above-mentioned eight hydroxides of alkali and alkaline earth metals in an aqueous solution can be written in the following way:

$$\begin{cases} \text{Alkali metal:} & \mathrm{AOH}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{A}^+(aq) + \mathrm{OH}^-(aq) \\ \text{Alkaline metal:} & \mathrm{M(OH)_2}(s) \xrightarrow{\mathrm{H_2O}} \mathrm{M}^{2+}(aq) + 2\,\mathrm{OH}^-(aq) \end{cases} \tag{9.6}$$

with A (M) representing the respective alkali (alkaline) metal. The other metal hydroxides are rather *insoluble* in an aqueous solution, so that they are designated as weak bases. For instance, the chemical reaction for the dissociation of the weak base beryllium hydroxide ($Be(OH)_2$) in water—this only happens to a very limited extent, given that this metal hydroxide is difficult to dissolve in water—looks as follows:

$$\mathrm{Be(OH)_2}(s) \rightleftharpoons \mathrm{Be^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \tag{9.7}$$

However, beryllium hydroxide ($Be(OH)_2$) does dissolve in either strong acid or alkali solutions. For example, in a solution of sodium hydroxide ($NaOH$), beryllium hydroxide ($Be(OH)_2$) reacts in the following manner:

$$\mathrm{Be(OH)_2}(s) + 2\,\mathrm{NaOH}(aq) \longrightarrow \mathrm{Na_2Be(OH)_4}(aq) \tag{9.8}$$

The difference between **dilute and concentrated solutions** equally applies in the context of bases. For example, we can have a dilute solution with a molarity of 0.15 $mol \cdot L^{-1}$ of the strong base potassium hydroxide (KOH), or a concentrated solution of 6.45 $mol \cdot L^{-1}$ of the weak base magnesium hydroxide ($Mg(OH)_2$).

Remember that the *weak-strong division* is indicating the extent to which ionization of a substance occurs in an aqueous solution, whereas the *dilute-concentrated range* refers to the amount of the acid or base that is incorporated within the solution.

Whereas non-metal oxides lead to acidic solutions when placed in contact with water, **basic solutions are created when *metal oxides* react with water**. The two below equations illustrate these reactions in the case of barium oxide (BaO) and sodium oxide (Na_2O):

$$\begin{array}{ll} \textit{Barium hydroxide} & \begin{cases} \mathrm{BaO}(s) + \mathrm{H_2O}(l) \longrightarrow \mathrm{Ba^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \\ \mathrm{Ba^{2+}}(aq) + 2\,\mathrm{OH^-}(aq) \longrightarrow \mathrm{Ba(OH)_2}(aq) \end{cases} \\ & \\ \textit{Sodium hydroxide} & \begin{cases} \mathrm{Na_2O}(s) + \mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Na^+}(aq) + 2\,\mathrm{OH^-}(aq) \\ \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NaOH}(aq) \end{cases} \end{array} \tag{9.9}$$

In fact, the metals that make up the eight strong bases are the only metals whose metal oxides are soluble in water, i.e., lithium oxide (Li_2O), sodium oxide (Na_2O), potassium oxide (K_2O), rubidium oxide (Rb_2O), cesium oxide (Cs_2O), calcium oxide (CaO), strontium oxide (SrO), and barium oxide (BaO).

In order to dissolve any other metal oxide, they are subjected to strong acidic or alkali solutions. For example, when aluminum oxide (Al_2O_3) is placed into a heated, concentrated solution of potassium hydroxide (KOH) in addition to water (H_2O), the solution potassium aluminate ($K[Al(OH)_4]$) is formed:

$$Al_2O_3(s) + 2\,KOH(aq) + 3\,H_2O(l) \longrightarrow 2\,K[Al(OH)_4](aq) \tag{9.10}$$

What is more, when a base and an acid in aqueous solution only differ from one another by the presence of a hydrogen cation (H^+), they are jointly known as a **conjugate acid-base pair**. In the below example, ammonia (NH_3) acts as a weak base, i.e., it absorbs a hydrogen ion (H^+), and pairs up with the conjugate acid ammonium (NH_4^+). At the same time, water (H_2O) behaves as a weak acid, i.e., it donates a hydrogen ion (H^+), and forms a conjugate acid-base pair with the hydroxide ion (OH^-).

$$\underset{\text{weak base}}{NH_3(g)} + \underset{\text{weak acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)} \tag{9.11}$$

Another example is the reaction between a hydrogen carbonate ion (HCO_3^-), which takes up the role of a weak acid, and water (H_2O), resulting in a carbonate ion (CO_3^{2-}) and a hydronium ion (H_3O^+):

$$\underset{\text{weak acid}}{HCO_3^-(aq)} + \underset{\text{weak base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate base}}{CO_3^{2-}(aq)} + \underset{\text{conjugate acid}}{H_3O^+(aq)} \tag{9.12}$$

Finally, in terms of **pH value**, a basic solution has a pH value **between 7 and 14**, while that of an acidic solution lies between 0 and 7. This means that the concentration of hydrogen ions (H^+) in a basic solution is lower compared to an acidic solution, or, put differently, the concentration of hydroxide ions (OH^-) is higher.

A basic solution is furthermore also referred to as an alkaline solution. In other words, the **acidity** of a solution increases when the pH value moves towards 0, whereas its **alkalinity** becomes more pronounced when progressing towards the pH value of 14.

As an example, let us calculate the pH value for a 3 L solution that contains 2.5 g of the strong base strontium hydroxide ($Sr(OH)_2$). The equivalent amount of mol is equal to $n_{(Sr(OH)_2)} = 2.1 \times 10^{-2}$ mol (with $M_r(Sr(OH)_2) = 121.64$ g$\cdot mol^{-1}$), so that $n_{(OH^-)} = 4.2 \times 10^{-2}$ mol. The molarity for hydroxide (per liter solution) is then calculated as $c_{(OH^-)} = [OH^-] = \frac{4.2\times10^{-2}}{3}\ mol \cdot L^{-1} = 1.37 \times 10^{-2}\ mol \cdot L^{-1}$.

Since it is experimentally established that the product of the concentration of the hydrogen and hydroxide ions always equals 10^{-14}, we find the concentration of hydrogen ions in our example as follows: $[H^+] = \frac{10^{-14}}{1.37\times10^{-2}} = 7.30 \times 10^{-13}$. Finally, this gives a pH value of $pH = -\log{(7.30 \times 10^{-13})} = -(\log{(7.30)} + \log{(10^{-13})}) = -(0.86 - 13) = 12.14$, indicating that the solution is very basic ($12.14 > 7$).

9.3 Salts

A **salt** is defined as an *ionic compound* that is the product of the reaction between an acid and a base, whereby the salt is formed by combining the *cation* of the base with the *anion* of the acid.

Apart from a salt, most of these acid-base reactions produce water and are referred to as **neutralization reactions**, which are typically *exothermic*, i.e., they give off heat. Put differently, neutralization reactions neutralize the acidity of the acid and the alkalinity of the base.

Let us consider Examples 3.5 and 3.6 from section 3.3, in which the salts strontium nitrate ($Sr(NO_3)_2$) and sodium sulfate (Na_2SO_4) are produced, respectively. In the case of $Sr(NO_3)_2$, it is fashioned from the cation of the base (Sr^{2+}) and the anion of the acid (NO_3^-). Similarly, Na_2SO_4 is synthesized by putting together the cation of the base (Na^+) and the anion of the acid (SO_4^{2-}).

$$\left\{\begin{array}{ccccccccc} \underset{\text{strong acid}}{2\,HNO_3(aq)} & + & \underset{\text{strong base}}{Sr(OH)_2(aq)} & \longrightarrow & \underset{\text{salt}}{Sr(NO_3)_2(aq)} & + & \underset{\text{water}}{2\,H_2O(l)} \\ \\ \underset{\text{strong acid}}{H_2SO_4(aq)} & + & \underset{\text{strong base}}{2\,NaOH(aq)} & \longrightarrow & \underset{\text{salt}}{Na_2SO_4(aq)} & + & \underset{\text{water}}{2\,H_2O(l)} \end{array}\right. \tag{9.13}$$

Other examples of neutralization reactions include the following equations, which form the salts calcium carbonate ($CaCO_3$), sodium phosphate (Na_3PO_4), iron(III) perchlorate ($Fe(ClO_4)_3$), and ammonium sulfate ($(NH_4)_2SO_4$), respectively:

$$\left\{\begin{array}{ccccccccc} \underset{\text{weak acid}}{H_2CO_3(aq)} & + & \underset{\text{strong base}}{Ca(OH)_2(aq)} & \longrightarrow & \underset{\text{salt}}{CaCO_3(s)} & + & \underset{\text{water}}{2\,H_2O(l)} \\ \\ \underset{\text{weak acid}}{H_3PO_4(aq)} & + & \underset{\text{strong base}}{3\,NaOH(aq)} & \longrightarrow & \underset{\text{salt}}{Na_3PO_4(aq)} & + & \underset{\text{water}}{3\,H_2O(l)} \\ \\ \underset{\text{strong acid}}{3\,HClO_4(aq)} & + & \underset{\text{weak base}}{Fe(OH)_3(s)} & \longrightarrow & \underset{\text{salt}}{Fe(ClO_4)_3(aq)} & + & \underset{\text{water}}{3\,H_2O(l)} \\ \\ \underset{\text{strong acid}}{H_2SO_4(aq)} & + & \underset{\text{weak base}}{2\,NH_4OH(aq)} & \longrightarrow & \underset{\text{salt}}{(NH_4)_2SO_4(aq)} & + & \underset{\text{water}}{2\,H_2O(l)} \end{array}\right. \tag{9.14}$$

Note that in section 9.2 we mentioned that weak bases are generally insoluble in water but soluble in strong acidic or alkaline solutions. We gave the example of the dissociation of beryllium hydroxide ($Be(OH)_2$) in an *alkali* solution (see Example 9.8). The third equation in Example 9.14 provides an example of a weak base ($Fe(OH)_3$) being dissolved in a strong *acidic* solution.

In all the examples above, the bases consist of **metal hydroxides** to form salts. However, salt can also be produced by means of substances other than metal hydroxides, such as **metal oxides**:

$$\begin{cases} \underset{\text{strong acid}}{2\,\mathrm{HCl}(aq)} + \underset{\text{metal oxide}}{\mathrm{Na_2O}(s)} \longrightarrow \underset{\text{salt}}{2\,\mathrm{NaCl}(aq)} + \underset{\text{water}}{\mathrm{H_2O}(l)} \\[2ex] \underset{\text{strong acid}}{6\,\mathrm{HI}(aq)} + \underset{\text{metal oxide}}{\mathrm{Al_2O_3}(s)} \longrightarrow \underset{\text{salt}}{2\,\mathrm{AlI_3}(aq)} + \underset{\text{water}}{3\,\mathrm{H_2O}(l)} \end{cases} \tag{9.15}$$

Also **carbonates** can give salts when reacted with strong acids, and besides water, these reactions additionally produce carbon dioxide gas (CO_2). A couple of examples are the following:

$$\begin{cases} \underset{\text{strong acid}}{2\,\mathrm{HNO_3}(aq)} + \underset{\text{carbonate}}{\mathrm{CaCO_3}(s)} \longrightarrow \underset{\text{salt}}{\mathrm{Ca(NO_3)_2}(aq)} + \underset{\text{water}}{\mathrm{H_2O}(l)} + \underset{\text{carbon dioxide}}{\mathrm{CO_2}(g)} \\[2ex] \underset{\text{strong acid}}{2\,\mathrm{HBr}(aq)} + \underset{\text{carbonate}}{\mathrm{BaCO_3}(s)} \longrightarrow \underset{\text{salt}}{\mathrm{BaBr_2}(aq)} + \underset{\text{water}}{\mathrm{H_2O}(l)} + \underset{\text{carbon dioxide}}{\mathrm{CO_2}(g)} \\[2ex] \underset{\text{strong acid}}{\mathrm{H_2SO_4}(aq)} + \underset{\text{carbonate}}{2\,\mathrm{NaHCO_3}(aq)} \longrightarrow \underset{\text{salt}}{\mathrm{Na_2SO_4}(aq)} + \underset{\text{water}}{2\,\mathrm{H_2O}(l)} + \underset{\text{carbon dioxide}}{2\,\mathrm{CO_2}(g)} \end{cases} \tag{9.16}$$

In above example 9.16, the reactant compounds based on carbonates are actually salts themselves. More specifically, they are salts composed of the anion of a weak acid, which in the case of Example 9.16 is the weak carbon acid (H_2CO_3).

Two more examples are provided below, whereby the *reactant* salts are based on the anion of the weak sulphurous acid (H_2SO_3) and phosphoric acid (H_3PO_4), respectively:

$$\begin{cases} \underset{\text{strong acid}}{2\,\mathrm{HClO_4}(aq)} + \underset{\text{sulfite}}{\mathrm{K_2SO_3}(aq)} \longrightarrow \underset{\text{salt}}{2\,\mathrm{KClO_4}(aq)} + \underset{\text{sulphur dioxide}}{\mathrm{SO_2}(g)} + \underset{\text{water}}{\mathrm{H_2O}(l)} \\[2ex] \underset{\text{strong acid}}{6\,\mathrm{HCl}(aq)} + \underset{\text{phosphate}}{\mathrm{Ca_3(PO_4)_2}(s)} \longrightarrow \underset{\text{salt}}{3\,\mathrm{CaCl_2}(aq)} + \underset{\text{phosphoric acid}}{2\,\mathrm{H_3PO_4}(aq)} \end{cases} \tag{9.17}$$

Salts are furthermore formed when **metals react with acids**, and the reaction will occur faster if strong acids are involved instead of weak acids. Moreover, these reactions typically produce hydrogen gas (H_2). The below examples include the reactive metals zinc (Zn), lithium (Li), aluminum (Al), and magnesium (Mg):

$$\left\{\begin{array}{ccccccc}
\underset{\text{strong acid}}{2\,HNO_3(aq)} & + & \underset{\text{metal}}{Zn(s)} & \longrightarrow & \underset{\text{salt}}{Zn(NO_3)_2(aq)} & + & \underset{\text{hydrogen gas}}{H_2(g)} \\[2ex]
\underset{\text{strong acid}}{2\,HBr(aq)} & + & \underset{\text{metal}}{2\,Li(s)} & \longrightarrow & \underset{\text{salt}}{2\,LiBr(aq)} & + & \underset{\text{hydrogen gas}}{H_2(g)} \\[2ex]
\underset{\text{weak acid}}{6\,HF(g)} & + & \underset{\text{metal}}{2\,Al(s)} & \longrightarrow & \underset{\text{salt}}{2\,AlF_3(s)} & + & \underset{\text{hydrogen gas}}{3\,H_2(g)} \\[2ex]
\underset{\text{weak acid}}{2\,CH_3COOH(aq)} & + & \underset{\text{metal}}{Mg(s)} & \longrightarrow & \underset{\text{salt}}{Mg(CH_3COO)_2(aq)} & + & \underset{\text{hydrogen gas}}{H_2(g)}
\end{array}\right. \tag{9.18}$$

Finally, the below examples consist of chemical reactions that give salts when **none of the reactants involved is an acid**. More specifically, salts can form when a metal oxide reacts with a non-metal oxide, a metal hydroxide with a non-metal oxide, a metal oxide with a salt, and a soluble salt with another soluble salt:

$$\left\{\begin{array}{ccccccccc}
\underset{\text{metal oxide}}{SrO(s)} & + & \underset{\text{non-metal oxide}}{SO_2(g)} & \longrightarrow & \underset{\text{salt}}{SrSO_3(s)} & & & & \\[2ex]
\underset{\text{metal hydroxide}}{KOH(s)} & + & \underset{\text{non-metal oxide}}{CO_2(g)} & \longrightarrow & \underset{\text{salt}}{KHCO_3(s)} & & & & \\[2ex]
\underset{\text{metal oxide}}{CaO(s)} & + & \underset{\text{salt}}{2\,NH_4NO_3(s)} & \longrightarrow & \underset{\text{salt}}{Ca(NO_3)_2(s)} & + & \underset{\text{ammonia}}{2\,NH_3(g)} & + & \underset{\text{water}}{H_2O(l)} \\[2ex]
\underset{\text{soluble salt}}{3\,AgNO_3(aq)} & + & \underset{\text{soluble salt}}{FeCl_3(aq)} & \longrightarrow & \underset{\text{salt}}{3\,AgCl(s)} & + & \underset{\text{salt}}{Fe(NO_3)_3(aq)} & &
\end{array}\right. \tag{9.19}$$

10 The Reaction Rate

10.1 A Definition

The speed at which a chemical reaction takes place until completion is known as the **reaction rate**. Put another way, the reaction rate is the rate at which reactants disappear and products are formed. The rate of the reaction can be *measured* by keeping track of the amount of a certain *physical property* of the reactant or product over time.

For any solid, liquid, or gas *in a solution*, the rate can be expressed as a change in **mass**, **temperature**, or **concentration** over time. Typically, the mass and concentration of the reactants (products) *decrease (increase)* as time evolves, while the direction of change in temperature depends on the nature of the chemical reaction. That is, an *exothermic* reaction releases heat, which is accompanied by an *increase* in temperature, whereas an *endothermic* reaction absorbs heat, thereby causing a *decline* in temperature (see section 11.2).

If a solution contains *light-absorbing reactants or products*, another physical property that can be measured is **colour**, since the amount of the respective substance, i.e., the concentration, will affect the colour intensity, the specific colour of the solution, or both. In the event that a reaction involves *gaseous substances*, the rate can furthermore be determined by measuring the evolution in **volume** or **pressure** of the reactants or products, following a change in the number of moles as the reaction progresses (see Equation 4.6 of the ideal gas law).

In the case that a solution consists of *ionic substances* (i.e., electrolytes; see section 12), another physical property that can be used to calculate the rate of the chemical reaction is the **electrical conductivity** of the solution, given that the extent to which the solution conducts electricity changes over time as the reaction develops.

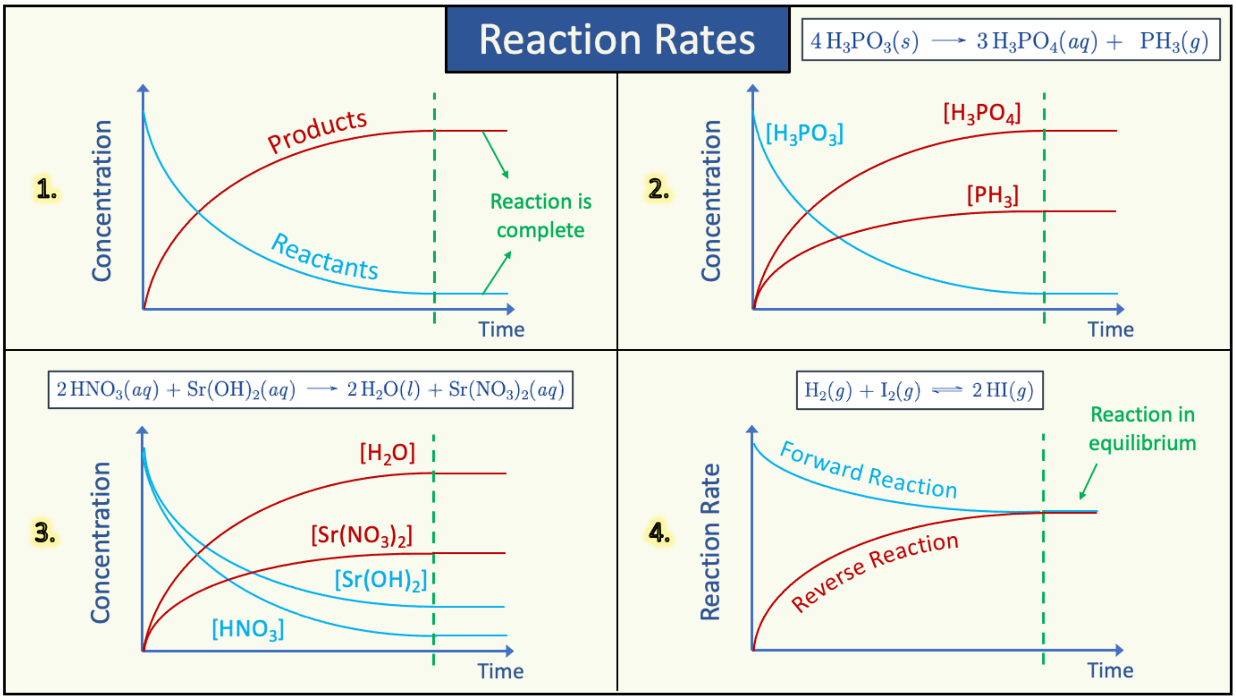


Figure 10.1: A graphical representation of reaction rates

Fig. 10.1 graphically demonstrates the evolution of the concentration of reactants and products as the chemical reaction proceeds—note that the reactants do not fully react away, as their final concentration is not equal to zero. Frame 1 illustrates a generic reaction whereby the concentration of the reactants (products) declines (increases) over time. At the moment that the reaction arrives at the green dotted line, the concentration remains constant, signaling that the reaction is completed.

Frame 2 and 3 provide two examples, whereby the reactant or product with a higher relative number of moles displays a larger gradient (i.e., a steeper curve). For instance, the reaction in Frame 3 produces 2 moles of water (H_2O) and 1 mole of strontium nitrate ($Sr(NO_3)_2$), resulting in a greater gradient for the [H_2O]-curve.

Frame 4 reflects the development of a reversible reaction. As the reaction starts going, the amount of concentration of the products is initially zero and builds up until the point where both the forward and the reverse reaction rate match each other (to the right of the green dotted line).

10.2 Influencing Factors

The particular rate of a reaction depends on the *nature* of the reactants and products as well as on the specific *conditions* in which the reaction occurs. This section discusses five factors that impact the reaction rate, i.e., concentration, temperature, reactant size, the presence of a catalyst, and pressure, and examines them from the perspective of **collision theory**. This theory regards the chemical reaction as a microscopic process of collisions and postulates, among other things, that *the reaction rate is proportional to the rate of collisions of the reactant substances.*

In terms of **concentration**, it is generally the case that a *higher* concentration of reactants *boosts* the reaction rate, since a greater number of substances (or a reduced volume for the same number of substances) enhances the likelihood of collisions among the substances and, therefore, the chances of initiating a chemical reaction. Concerning the **temperature**, an *increase* in temperature, which is defined as the average of the kinetic energies of all the individual atoms or molecules that make up a reactant, equally *augments* the reaction rate, given that faster moving substances improve their frequency of collisions.

Another element that affects the reaction rate is the **size of the reactant**. With respect to a soluble solid that reacts with a solvent, a *smaller* size *stimulates* the reaction rate, because many small particles are equivalent to a larger *aggregated* surface area with which the solvent can react. In contrast, a larger size of the reactant—and thus a fewer number of substances—implies a reduced aggregate surface area, and thus diminishes the reaction rate.

What is more, the presence of a **catalyst**, which is a substance that is added to the reaction and facilitates an alternative reaction mechanism without itself being chemically altered (see section 10.4), *speeds up* the reaction. Finally, when it comes to the influence of **pressure** in the context of gases, a *greater* amount of pressure (at a constant temperature) results in a smaller volume in which the gas is contained (see section 4.4.1), which in turn leads to *higher* frequency of collisions of the individual substances and thus a higher likelihood of an improved reaction rate.

To understand how the *equilibrium* of a reversible chemical reaction is being restored under the influence of changes in temperature, pressure, or concentration, please refer to section 3.4, which delves into Le Chatelier's principle.

10.3 Activation Energy

A higher frequency of collisions does not necessarily result in an increased reaction rate. Apart from a greater number of collisions and an appropriate orientation of the individual substances, an additional requirement for a chemical reaction to occur is that the reactant substances must possess a certain minimal amount of energy to effectively kick off the reaction. This energy is referred to as the **activation energy** $E_{\mathbf{A}}$.

Regardless of whether the reaction is exothermic or endothermic, an activation energy is required for the reactants to (partially) break their chemical bonds. Once the reactant substances absorb this activation energy, they end up in a so-called higher-energy **transition state**, after which the reactants can proceed to form products.

The *source* of the activation energy is typically heat in the form of a higher average kinetic energy of the reactants—this is the definition of temperature. Therefore, an *increase* in temperature enhances the frequency of collisions of reactant substances *that have sufficient energy*—this is the activation energy—to kickstart the chemical reaction. This effect of temperature on the reaction rate is illustrated by the graph on the left-hand side in Fig. 10.2.

The two graphs on the right-hand side in Fig. 10.2 depict the concept of activation energy, which is often indicated by the notation $\Delta E^{\ddagger}$, for an exothermic and endothermic reaction.

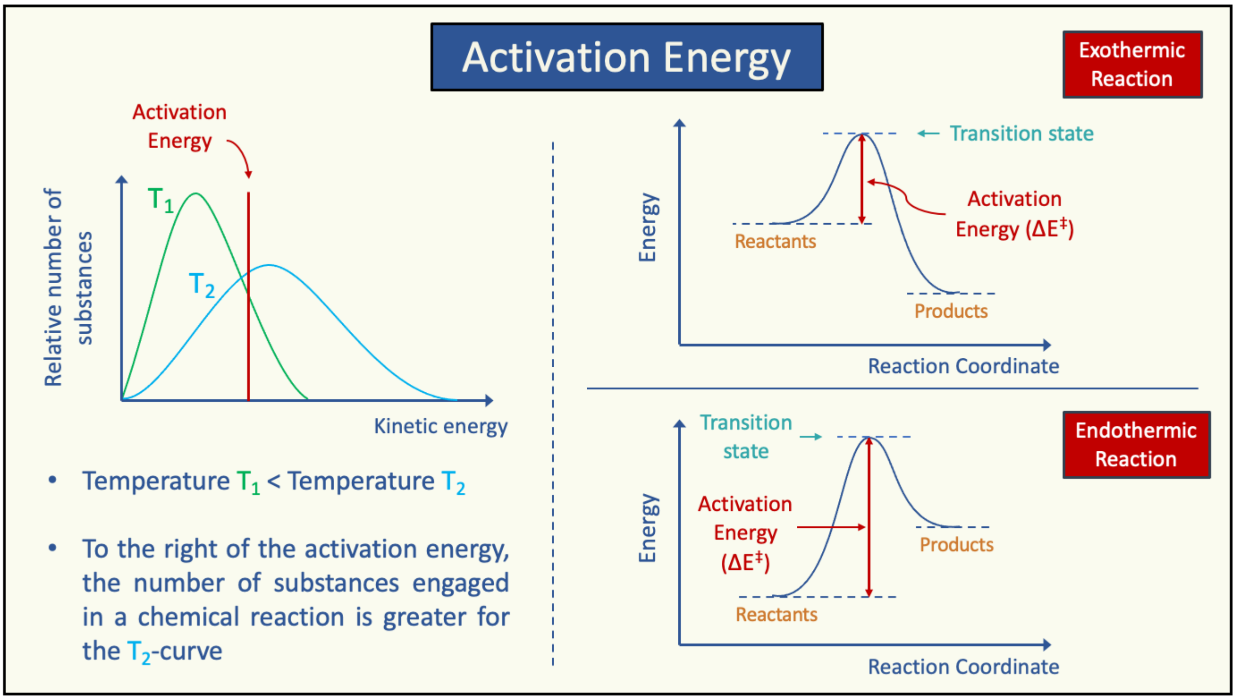


Figure 10.2: A schematic overview of activation energy

10.4 Catalysts

As mentioned in section 10.2, a **catalyst** is a substance that is added to the chemical reaction to *enhance* the reaction rate. This improved rate is achieved by introducing a new reaction mechanism that is energetically more favourable. In other words, a catalyst *lowers* the activation energy E_A of the reaction, so that a greater number of substances can become involved in the chemical reaction—this would correspond to moving the vertical red line in the graph at the left-hand side in Fig. 10.2 *to the left*, which is shown in Fig. 10.3.

Another characteristic of a catalyst is the fact that the reaction *does not consume* the catalytic substance. This means that the catalyst is *not chemically altered* at the end of the reaction and, moreover, that only a *small amount* of the substance is sufficient to catalyze the reaction many times over.

In the context of reversible reactions, a catalyst has the additional property that it *does not impact the equilibrium position*, since it affects the forward and reverse reaction in an equal manner.

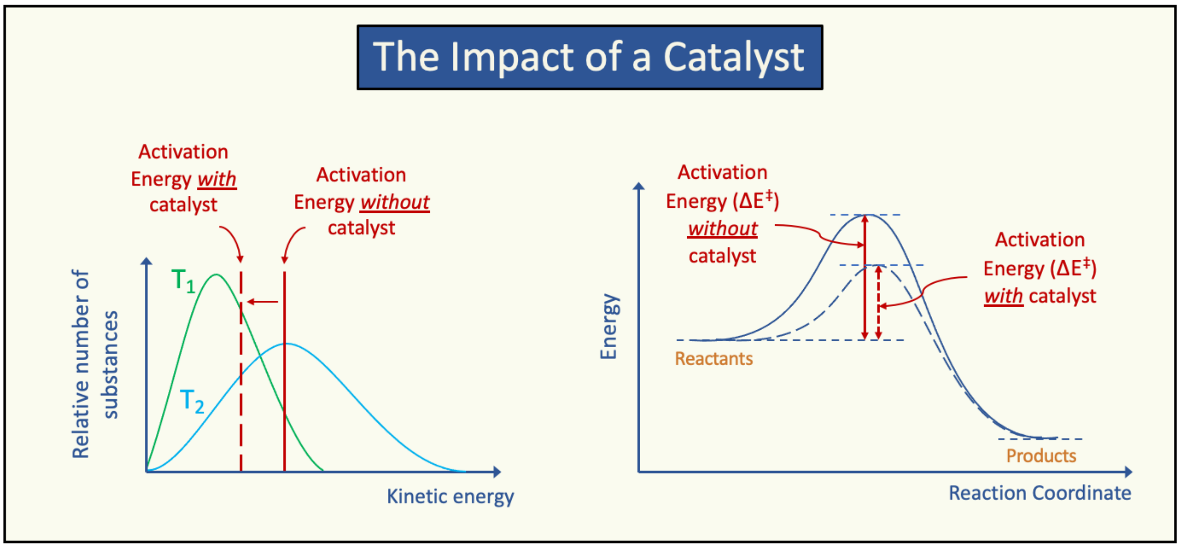


Figure 10.3: The effect of a catalyst on the activation energy

An example of a catalytic reaction is the decomposition of hydrogen peroxide (H_2O_2) into water (H_2O) and oxygen gas (O_2)—this is a disproportionation reaction (see section 5.4)—by adding the catalyst manganese dioxide (MnO_2). In a first step, MnO_2 acts as an oxidizing agent, thereby oxidizing H_2O_2 to O_2. In a second phase, the manganese(II) ion (Mn^{2+}) takes up the role of reducing agent and reacts with H_2O_2 to form the original catalytic compound MnO_2. The respective chemical reactions are the following:

$$\begin{cases} \text{Initial equation:} & 2\,H_2O_2(aq) \xrightarrow{MnO_2} 2\,H_2O(l) + O_2(g) \\ 1^{st}\text{ step:} & MnO_2(s) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l) + O_2(g) \\ 2^{nd}\text{ step:} & Mn^{2+}(aq) + H_2O_2(aq) \longrightarrow MnO_2(s) + 2\,H^+(aq) \end{cases} \tag{10.1}$$

11 Energetics

11.1 Bond Energy

The amount of heat energy that a substance possesses is referred to as **enthalpy**, denoted by the letter H. In addition, the amount of energy (enthalpy) it takes to break a bond between two elements is known as the **bond dissociation enthalpy or bond energy**, indicated by the notation ΔH_b. Given that energy must be *supplied* to the substance in order to break a chemical bond, it follows that the bond energy ΔH_b is *always positive*. Note that when the bond energy is measured at the standard state, i.e., at 25°C and at atmospheric pressure, it is written as ΔH_b°.

Table 11.1: The bond dissociation enthalpy ΔH_b° (in kJ·mol^{-1}) of different bonds

Single Bonds				**Multiple Bonds**			
Bond	ΔH_b° (in kJ·mol^{-1})	**Bond**	ΔH_b° (in kJ·mol^{-1})	**Bond**	ΔH_b° (in kJ·mol^{-1})	**Bond**	ΔH_b° (in kJ·mol^{-1})
H−H	436.0	**H−N**	389.1	**C=C**	610.9	**C≡C**	836.8
C−C	347.3	**H−O**	464.4	**N=N**	456.1	**N≡N**	945.6
N−N	160.7	**H−Cl**	431.0	**O=O**	497.9	$\mathbf{CH_3{\equiv}CH_3}$	962.3
O−O	146.4	**H−Br**	366.1	**C=N**	615.0	**C≡N**	891.2
Cl−Cl	242.7	**H−F**	564.8	**C=O**	803.3	**C≡O**	1,079.5
H−C	414.2	**H−S**	338.9	**S=O**	535.6	**P≡P**	489.5

What is more, the **atomization energy** is the sum of all the bond dissociation enthalpies of a molecule and is thus defined as the energy required to break apart that molecule or compound into its individual elements, i.e., its *atomized* state.

11.2 Reaction Energetics

Based on the definitions in section 11.1, the **enthalpy change of a chemical reaction**, which is denoted by ΔH_r, can be defined as the difference between the total bond dissociation enthalpies of the reactants minus that of the products. Alternatively, the change in enthalpy of a chemical reaction ΔH_r can also be described as the difference between the enthalpy of the products and that of the reactants. The following definitions are equivalent:

$$\begin{aligned}
\Delta H_r &= \sum atomization\ energy\ reactants &&- \sum atomization\ energy\ products \\
&= \sum bond\ energies\ reactants &&- \sum bond\ energies\ products \\
&= \sum bond\ energies\ of\ broken\ bonds &&- \sum bond\ energies\ of\ formed\ bonds \\
&= H_{Products} - H_{Reactants}
\end{aligned} \tag{11.1}$$

Fig. 11.1 illustrates the change in enthalpy for the formation of ethane C_2H_6 (left-hand side) and the oxidation of glucose $C_6H_{12}O_6$ (right-hand side). In the first case, the sum of the bond dissociation enthalpies of all the reactants ($\sum \Delta H^\circ_{b\,(\text{reactants})}$) is larger than that of the products, resulting in a *positive* enthalpy change ($\Delta H^\circ_r > 0$). In other words, the production of ethane according to this reaction *requires an inflow* of heat energy from the environment, as it takes more energy to break up the bonds of the reactants with respect to the atomization energy of the formed products.

We witness the opposite scenario for the oxidation of glucose. That is, the sum of the bond energies of the products ($\sum \Delta H^\circ_{b\,(\text{products})}$) is larger compared to that of the reactants, so that the enthalpy change turns out to be *negative* ($\Delta H^\circ_r < 0$). Put differently, a lower enthalpy level of the products ($H_{Products}$) implies that this reaction is *giving off* heat energy to its environment.

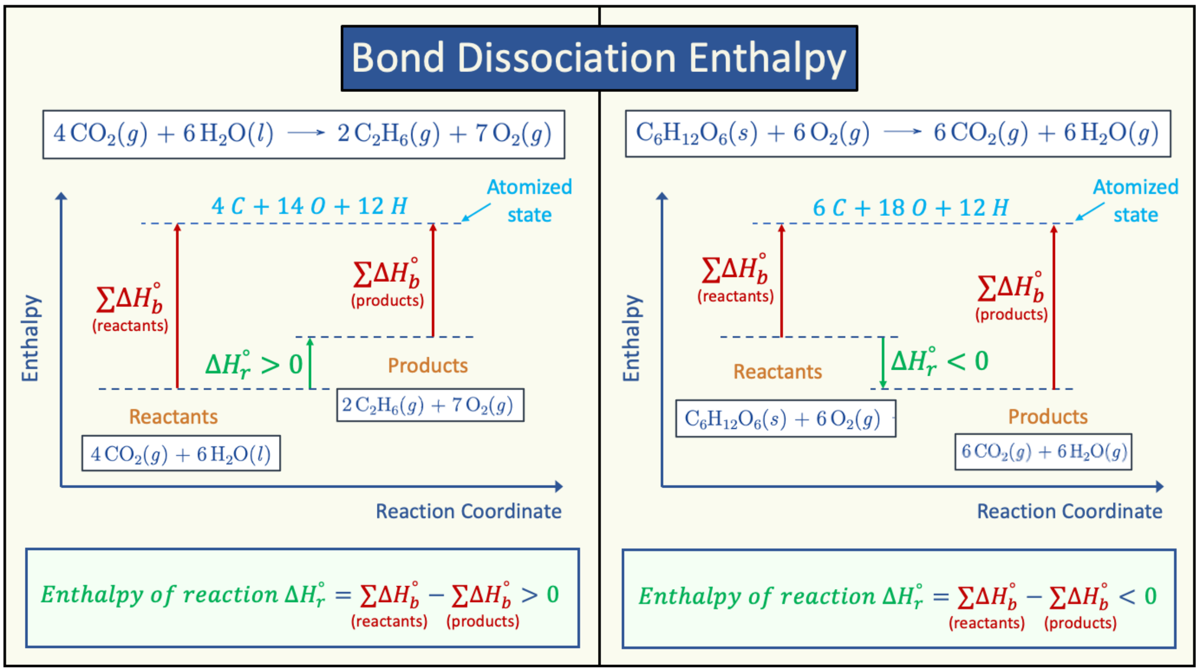


Figure 11.1: A schematic view of the change in enthalpy of a chemical reaction

As a matter of fact, a chemical reaction that provides heat energy to its environment is referred to as an **exothermic reaction**. Put another way:

$$\begin{aligned} \textit{A reaction is exothermic} \quad &\Leftrightarrow \quad \Delta H_r < 0 \\ &\Leftrightarrow \quad \sum \Delta H_{b\,(reactants)} < \sum \Delta H_{b\,(products)} \qquad (11.2) \\ &\Leftrightarrow \quad H_{Products} < H_{Reactants} \end{aligned}$$

Similarly, an **endothermic reaction** is a chemical reaction that requires an input of heat energy from the environment in order to bring the reaction to completion. In mathematical notation, this is equivalent to:

$$\begin{aligned} \textit{A reaction is endothermic} \quad &\Leftrightarrow \quad \Delta H_r > 0 \\ &\Leftrightarrow \quad \sum \Delta H_{b\,\textit{(reactants)}} > \sum \Delta H_{b\,\textit{(products)}} \qquad (11.3) \\ &\Leftrightarrow \quad H_{Products} > H_{Reactants} \end{aligned}$$

Both Fig. 10.2 and Fig. 11.1 teach us that breaking (forming) a chemical bond is *always* endothermic (exothermic) in nature, regardless of whether we are dealing with an endothermic or exothermic reaction—remember that the distinction between these two types of reaction is only determined by the relative position of their initial and final enthalpy.

In the case of a **reversible reaction**, there exists a symmetry in terms of their thermal properties. That is to say, if, for instance, the forward reaction is endothermic, then the reverse reaction will be exothermic, and vice versa. An example is chemical reaction 3.12 whereby hydrogen gas (H_2) reacts with iodine (I_2) to form hydrogen iodide (HI):

$$\begin{cases} \text{The reversible reaction:} & H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + \textit{heat} \\ \text{The forward reaction is exothermic:} & H_2(g) + I_2(g) \longrightarrow 2\,HI(g) + \textit{heat} \\ \text{The reverse reaction is endothermic:} & 2\,HI(g) + \textit{heat} \longrightarrow H_2(g) + I_2(g) \end{cases} \qquad (11.4)$$

11.3 Calculations

Let us now delve into the numbers and actually calculate the change in enthalpy of chemical reactions. As per definition 11.1, we obtain the change in enthalpy by subtracting the total sum of the bond energies of the products from that of the reactants. In a first example, methane (CH_4) is burnt whereby carbon dioxide (CO_2) and water (H_2O) are formed:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) \qquad (11.5)$$

Since CH_4 consists of four single bonds, O_2 of a double bond, CO_2 of two double bonds, and H_2O of two single bonds, we know from Table 11.1 that ΔH_b° (C−H) = 414.2 kJ·mol^{-1}, ΔH_b° (O=O) = 497.9 kJ·mol^{-1}, ΔH_b° (C=O) = 803.3 kJ·mol^{-1}, and ΔH_b° (H−O) = 464.4 kJ·mol^{-1}.

Therefore, the change in enthalpy of the burning of methane is equal to $\Delta H_r^\circ = (4 \times 414.2 + 2 \times 497.9) - (2 \times 803.3 + 4 \times 464.4)$ kJ·mol^{-1} = -811.6 kJ·mol^{-1}. In other words, the reaction as per Equation 11.5 is exothermic ($\Delta H_r^\circ < 0$).

As a second example, let us take the formation of ethane (C_2H_6) as discussed in Fig. 11.1 (left-hand side):

$$4\,CO_2(g) + 6\,H_2O(l) \longrightarrow 2\,C_2H_6(g) + 7\,O_2(g) \tag{11.6}$$

The relevant enthalpy information for the compounds CO_2 and H_2O and the molecule O_2 can be found in the previous example. Regarding the compound C_2H_6, its molecular structure looks as follows:

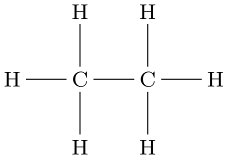


Figure 11.2: The molecular structure of ethane (C_2H_6)

This means that C_2H_6 contains one single bond C−C and six single bonds C−H, whereby ΔH_b° (C−C) = 347.3 kJ·mol^{-1} (that of the bond C−H is given in the previous example). Therefore, the change in enthalpy is equal to $\Delta H_r^\circ = (8 \times 803.3 + 12 \times 464.4) - (2 \times 347.3 + 12 \times 414.2 + 7 \times 497.9)$ kJ·mol^{-1} = $2,848.9$ kJ·mol^{-1}. However, the change in enthalpy is measured per *one unit of mol*, whereas in reaction 11.6 there are *two* moles of ethane. As a result, the enthalpy change of the formation of ethane is equal to $\Delta H_r^\circ = \frac{2{,}848.9}{2}$ kJ·mol^{-1} = $1,424.5$ kJ·mol^{-1}. Put differently, the formation of ethane is endothermic ($\Delta H_r^\circ > 0$).

In a final example, we examine the oxidation of glucose ($C_6H_{12}O_6$), which is already studied to some extent in Fig. 11.1 (right-hand side):

$$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(g) \tag{11.7}$$

The molecular structure of glucose has the following form (the free electron pairs of oxygen are not shown here):

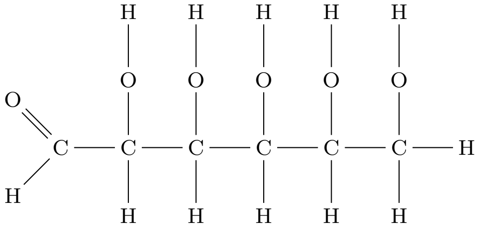


Figure 11.3: The molecular structure of glucose ($C_6H_{12}O_6$)

Given that ΔH_b° (C$-$O) = 357.7 kJ$\cdot$mol^{-1} (the enthalpy information of the other bonds are mentioned in the previous examples), we calculate the change in enthalpy as $\Delta H_r^\circ = (1 \times 803.3 + 7 \times 414.2 + 5 \times 347.3 + 5 \times 357.7 + 5 \times 464.4 + 6 \times 497.9) - (12 \times 803.3 + 12 \times 464.4)$ kJ$\cdot$mol^{-1} = $-2,675.3$ kJ$\cdot$mol^{-1}. Based on this result, we conclude that the oxidation of glucose is an exothermic process ($\Delta H_r^\circ < 0$), which corresponds to Fig. 11.1 (right-hand side) where indeed $H_{Products} < H_{Reactants}$.

12 Electrolysis

12.1 A Definition

An **electrochemical cell** consists of two electrically conducting elements called **electrodes**—these are usually metal plates or wires—that are placed in a solution of **electrolytes**, i.e., aqueous anions (negatively charged ions) and cations (positively charged ions).

The objective of an electrochemical cell entails the conversion between chemical and electrical energy. That is, **voltaic or galvanic electrochemical cells**, which are used in batteries, rely on chemical reactions to generate an electric current, whereas **electrolytic cells** draw from the flow of electrons issued by a voltage source to drive non-spontaneous chemical reactions. In other words, electrolysis is the *reverse* of the processes taking place in galvanic cells.

The **anode** is the electrode of an electrochemical cell that engages in an *oxidation reaction*, while the **cathode** is the electrode that undergoes a *reduction reaction* (see section 5.2 for more details on redox reactions). Put differently, the anode produces electrons, leaving cations behind, whereas the cathode receives electrons, turning cations into neutral elements.

Note that in a galvanic cell the anode (cathode) is defined as the minus (–) side (plus (+) side) of the cell, while in an electrolytic cell this is reversed, i.e., the anode makes up the plus (+) side and the cathode the minus (–) side of the cell. The remainder of this chapter focuses exclusively on electrolytic cells.

In **electrolysis**, an external power source, e.g., a battery, is connected by wires to the electrodes of the electrolytic cell—the anode (–) (cathode (+)) of the battery is coupled to the cathode (–) (anode (+)) of the electrolytic cell—to drive electrons through the cell. As a result, the battery instructs the electrolytic cathode to consume the electrons (reduction) and the anode to release electrons (oxidation). Keep in mind that a *direct* current is used rather than an alternating current, because otherwise the electrode materials would constantly switch roles between anode and cathode and therefore fail to properly oxidize or reduce the substances.

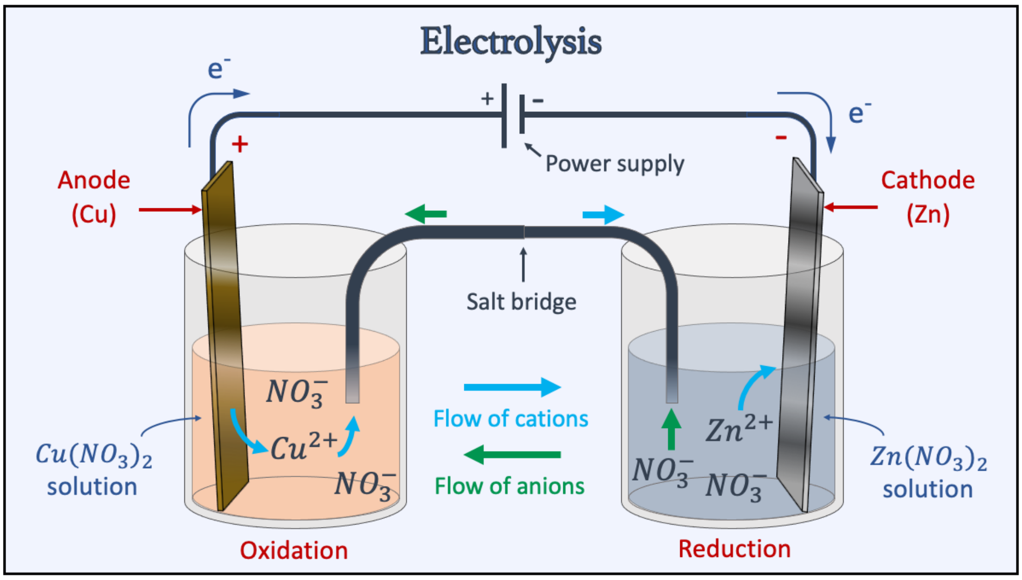


Figure 12.1: One possible configuration of an electrolytic cell

Take the example of zinc (Zn) and copper (Cu), whereby zinc (Zn) is the stronger *reducing* agent, i.e., copper (Cu) gets reduced while zinc (Zn) is oxidized (see Table 12.1). This means that in an electrochemical cell *without* a connected power supply, the electrons would flow from a negative Zn anode to a positive Cu cathode.

The electrolytic cell in Fig. 12.1 illustrates a possible set-up of the *reversed* process whereby copper (Cu) is now forced to take on the role of the stronger reducing agent—the Cu atoms continuously donate their electrons due to the constant pull exerted on the electrons by the positive side of the installed power source—and whereby the metal solutions, i.e., copper nitrate ($Cu(NO_3)_2$) and zinc nitrate ($Zn(NO_3)_2$), are not allowed to mingle.

To ensure the flow of electrons in this cell, a so-called **salt bridge** is installed between the two beakers. Note that the salt bridge can be a piece of cloth or a cord, which is soaked in an ionic solution, e.g., sodium nitrate ($NaNO_3$). In short, the salt bridge allows the free travel of nitrate (NO_3^-) and sodium (Na^+) ions between the two beakers, but restricts the flow of the ions involved in the redox reactions, i.e., copper (Cu^{2+}) and zinc (Zn^{2+}).

More precisely, the salt bridge supports the electron flow by, on the one hand, releasing sodium cations (Na^+) in the $Zn(NO_3)_2$ solution in case that an excess of electrons gather on the cathode—remember that an accumulation of electrons would repel further incoming electrons and reduce the electron flow—because the Na^+ cations would neutralize the NO_3^- ions, leaving behind a relatively greater amount of Zn^{2+} ions, which would in turn consume the excess of electrons.

At the other hand, the salt bridge sends NO_3^- anions into the $Cu(NO_3)_2$ solution to ensure the electron flow in the circuit. Moreover, the salt bridge prevents Cu^{2+} cations from migrating to the cathode, where they would get reduced instead of the Zn^{2+} cations—keep in mind that zinc (Zn) is the stronger reducing agent of the two. The Na^+ cations do not pose this problem, since sodium (Na) is a stronger reducing agent than zinc (Zn), as per Table 12.1.

The oxidation and reduction reaction at the respective electrode as well as the overall net equation of the electrolytic process take the following form:

$$\begin{cases} \text{Reduction (cathode):} & Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) \\ \text{Oxidation (anode):} & Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^- \\ \text{Net cell reaction:} & Zn^{2+}(aq) + Cu(s) \longrightarrow Zn(s) + Cu^{2+}(aq) \end{cases} \tag{12.1}$$

12.2 Molten and Aqueous Conditions

Electrolysis under molten and aqueous solutions of the *same* ionic compound does not give the same products, since water also plays a role in the case of aqueous solutions. Let us first consider **molten compounds**.

When ionic compounds, such as sodium chloride (NaCl), tungsten(IV) chloride (WCl_4), potassium bromide (KBr), or lithium fluoride (LiF), dissociate into their respective ions when molten, the cations will be attracted towards the cathode (–) and the anions towards the anode (+) of the electrolytic cell—in this set-up, no salt bridge is present. This means that the cation is reduced, while the anion is oxidized.

In other words, electrolysis of a molten ionic compound, which is basically a salt, produces *the individual elements of the compound*, i.e., the (liquid) metal and the (gaseous) non-metallic element. For instance, electrolysis of molten lithium fluoride (LiF) gives the metal lithium (Li) in liquid form and fluorine gas (F_2). The corresponding half-equations and the net reaction are the following:

$$\begin{cases} \text{Reduction (cathode):} & \mathrm{Li^+}(l) + \mathrm{e^-} \longrightarrow \mathrm{Li}(l) \\ \text{Oxidation (anode):} & 2\,\mathrm{F^-}(l) \longrightarrow \mathrm{F_2}(g) + 2\,\mathrm{e^-} \\ \text{Net cell reaction:} & 2\,\mathrm{Li^+}(l) + 2\,\mathrm{F^-}(l) \longrightarrow 2\,\mathrm{Li}(l) + \mathrm{F_2}(g) \end{cases} \tag{12.2}$$

Another example is the electrolysis of molten sodium chloride (NaCl), which generates the liquid metal sodium (Na) and the toxic gas chlorine (Cl_2):

$$\begin{cases} \text{Reduction (cathode):} & \mathrm{Na^+}(l) + \mathrm{e^-} \longrightarrow \mathrm{Na}(l) \\ \text{Oxidation (anode):} & 2\,\mathrm{Cl^-}(l) \longrightarrow \mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \\ \text{Net cell reaction:} & 2\,\mathrm{Na^+}(l) + 2\,\mathrm{Cl^-}(l) \longrightarrow 2\,\mathrm{Na}(l) + \mathrm{Cl_2}(g) \end{cases} \tag{12.3}$$

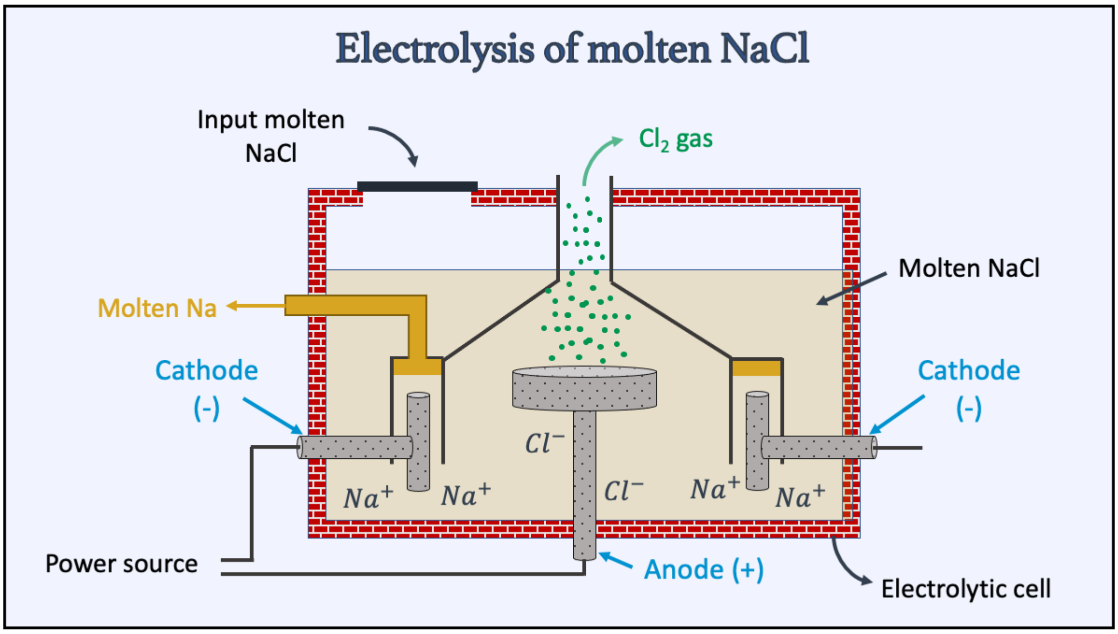


Figure 12.2: Electrolysis of molten NaCl

If we are dealing with a **mixture of molten salts**, the *electronegativity* of the elements will be instructive to determine which products come out of the electrolytic process. That is, at the respective electrode, the element with the *highest* electronegative value takes up the role of the *stronger oxidizing agent*, since it has a greater tendency to attract electrons—remember that, overall, electronegativity increases higher up a Group and to the right within a Period in the Periodic Table (see section 5.3).

For instance, given a mixture of the two molten salts strontium bromide ($SrBr_2$) and rubidium iodide (RbI), the two competing cations at the cathode are Sr^{2+} and Rb^+, whereas the anode attracts the two anions Br^- and I^-. With respect to the cathode, since strontium possesses a slightly larger electronegative value—it belongs to Group 2, while rubidium (Rb) resides in Group 1—it acts as the stronger oxidizing agent. As a result, liquid strontium (Sr) is produced at the cathode.

Similarly, given that bromide (Br^-) takes up the role as the stronger oxidizing agent—bromine (Br) sits higher up in Group 17 compared to iodine (I) and has thus a larger electronegative value—it follows that iodine gas (I_2) is formed at the anode. The chemical reactions are the following:

$$\begin{cases} \text{Reduction (cathode):} & \mathrm{Sr^{2+}}(l) + 2\,\mathrm{e^-} \longrightarrow \mathrm{Sr}(l) \\ \text{Oxidation (anode):} & 2\,\mathrm{I^-}(l) \longrightarrow \mathrm{l_2}(g) + 2\,\mathrm{e^-} \\ \text{Net cell reaction:} & \mathrm{Sr^{2+}}(l) + 2\,\mathrm{I^-}(l) \longrightarrow \mathrm{Sr}(l) + \mathrm{I_2}(g) \end{cases} \tag{12.4}$$

Another example is the molten mixture of sodium chloride (NaCl) and aluminum fluoride (AlF_3). At the cathode, aluminum (Al^{3+}) is the stronger oxidizing agent, whereas fluoride (F^-) takes up that role at the anode. This results in the following half-equations and the net overall reaction of the electrolysis of this particular mixture:

$$\begin{cases} \text{Reduction (cathode):} & \mathrm{Al^{3+}}(l) + 3\,\mathrm{e^-} \longrightarrow \mathrm{Al}(l) \\ \text{Oxidation (anode):} & 2\,\mathrm{CI^-}(l) \longrightarrow \mathrm{C_2}(g) + 2\,\mathrm{e^-} \\ \text{Net cell reaction:} & 2\,\mathrm{Al^{3+}}(l) + 6\,\mathrm{CI^-}(l) \longrightarrow 2\,\mathrm{Al}(l) + 3\,\mathrm{CI_2}(g) \end{cases} \tag{12.5}$$

Let us now turn to electrolysis in **aqueous solutions**. First consider that every half-reaction comes with their own **standard electrode potential**, denoted by E° (expressed in Volt (V) and measured at the standard state), which is a form of stored energy, i.e., potential energy, related to the valence electrons of an element *relative to* that of the element hydrogen. That is, the standard electrode potential, which refers to a *difference* in potential energy, is the reason why electrons flow.

The products of electrolysis under aqueous conditions can be predicted by the following **rule of thumb**: the half-reaction with the *higher* E° value is the *stronger oxidizing agent* and will take place at the *cathode*, whereas the half-reaction with the *lower* E° value is the *stronger reducing agent* and will take place at the *anode*.

Table 12.1 provides a couple of half-equations for which the standard electrode potential E° is measured:

Table 12.1: The standard electrode potential E° of some half-reactions

Half-Reaction	**E° (V)**
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Al^{3+}(aq) + 3\,e^- \rightleftharpoons Al(s)$	-1.68
$2\,H_2O(l) + 2\,e^- \rightleftharpoons H_2(g) + 2\,OH^-(aq)$	-0.83
$Zn^{2+}(aq) + 2\,e^- \rightleftharpoons Zn(s)$	-0.76
$2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + 2\,e^- \rightleftharpoons Cu(s)$	0.34
$Cl_2(g) + 2\,e^- \rightleftharpoons 2\,Cl^-(aq)$	1.36
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightleftharpoons 2\,H_2O(l)$	1.4

In the case of the electrolysis of aqueous sodium chloride (NaCl), we first list the possible half-reactions per electrode together with their corresponding E° value:

$$\begin{aligned}
&\textit{Cathode} \quad \begin{cases} Na^+(aq) + e^- \longrightarrow Na(s) & (E^\circ = -2.71) \\ 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) & (E^\circ = -0.83) \end{cases} \\
&\textit{Anode} \quad \begin{cases} 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- & (E^\circ = 1.36) \\ 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- & (E^\circ = 1.4) \end{cases}
\end{aligned} \tag{12.6}$$

Applying the above-mentioned rule of thumb, it follows that water (H_2O) is the stronger oxidizing agent at the cathode ($E^\circ_{H_2O} > E^\circ_{Na^+}$), while chloride ($Cl^-$) is the stronger reducing agent at the anode ($E^\circ_{Cl^-} < E^\circ_{H_2O}$). In other words, water is reduced at the cathode and chloride is oxidized at the anode (see Fig. 12.3 below). The net ionic equation then becomes:

$$2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2\,OH^-(aq) \tag{12.7}$$

Comparing with NaCl electrolysis under *molten* conditions (see Equation 12.3), which delivers molten sodium (Na) and chlorine gas (Cl_2), we can observe from Equation 12.7 that the products are different in the case of NaCl electrolysis under *aqueous* conditions.

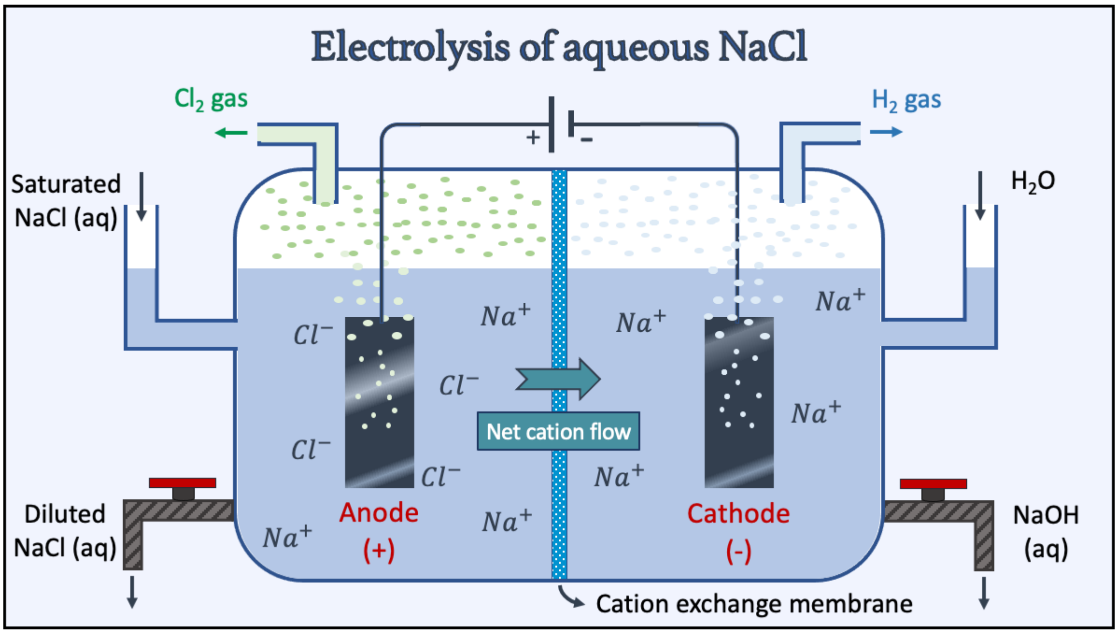


Figure 12.3: Electrolysis of aqueous NaCl

Another example examines the electrolysis of a copper(II) nitrate ($Cu(NO_3)_2$) solution, whereby the possible half-reactions per electrode include (bear in mind that the nitrate anion (NO_3^-) cannot be further oxidized):

$$\begin{aligned}
&\textit{Cathode} \quad \begin{cases} Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) & (E^\circ = 0.34) \\ 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) & (E^\circ = -0.83) \end{cases} \\
&\textit{Anode} \quad \begin{cases} 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \quad (E^\circ = 1.4) \end{cases}
\end{aligned} \tag{12.8}$$

In other words, copper (Cu^{2+}) is the stronger oxidizing agent at the cathode, whilst water (H_2O) is the substance that will be oxidized at the anode. As a result, we obtain the following net ionic equation for this electrolytic process:

$$2\,Cu^{2+}(aq) + 2\,H_2O(l) \longrightarrow 2\,Cu(s) + O_2(g) + 4\,H^+(aq) \tag{12.9}$$

The same rule of thumb applies when considering an **aqueous mixture of various salts**. For example, the different possible half-reactions at the respective electrode for an aqueous mixture of strontium iodide (SrI_2) and ferrous sulfate ($FeSO_4$) are the following (note that the sulfate anion (SO_4^{2-}) cannot be further oxidized):

$$\begin{aligned}
&\textit{Cathode} \quad \begin{cases} Sr^{2+}(aq) + 2\,e^- \longrightarrow Sr(s) & (E^\circ = -2.90) \\ Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s) & (E^\circ = -0.41) \\ 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) & (E^\circ = -0.83) \end{cases} \\
&\textit{Anode} \quad \begin{cases} 2\,I^-(aq) \longrightarrow I_2(g) + 2\,e^- & (E^\circ = 0.54) \\ 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- & (E^\circ = 1.4) \end{cases}
\end{aligned} \tag{12.10}$$

These potential values imply that iron (Fe^{2+}) is the stronger oxidizing agent at the cathode whereas iodine (I^-) takes up the role of the stronger reducing agent at the anode, which means that iron metal (Fe) is being deposited at the cathode and iodine gas (I_2) is produced at the anode. The net ionic equation can be written as follows:

$$Fe^{2+}(aq) + 2\,I^-(aq) \longrightarrow Fe(s) + I_2(g) \tag{12.11}$$

A second example involves the aqueous mixture of sodium chloride (NaCl) and potassium phosphate (K_3PO_4), which gives the following possible half-reactions (keep in mind that the phosphate anion (PO_4^{3-}) cannot be further oxidized):

$$\begin{aligned}
&\textit{Cathode} \quad \begin{cases} Na^+(aq) + e^- \longrightarrow Na(s) & (E^\circ = -2.71) \\ K^+(aq) + e^- \longrightarrow K(s) & (E^\circ = -2.93) \\ 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) & (E^\circ = -0.83) \end{cases} \\
&\textit{Anode} \quad \begin{cases} 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- & (E^\circ = 1.36) \\ 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- & (E^\circ = 1.4) \end{cases}
\end{aligned} \tag{12.12}$$

Given that water (H_2O) is reduced at the cathode and chlorine (Cl^-) is oxidized at the anode, we obtain the following net ionic equation:

$$2\,H_2O(l) + 2\,Cl^-(aq) \longrightarrow H_2(g) + 2\,OH^-(aq) + Cl_2(g) \tag{12.13}$$

12.3 Electrolysis of Water

The dissociation of water (H_2O) into its elements, i.e., oxygen gas (O_2) and hydrogen gas (H_2), is a non-spontaneous chemical reaction. That is, the decomposition of water by means of thermal energy takes place with the addition of extremely large amounts of heat (at temperatures between 2,200°C and 3,000°C).

When turning to the method of electrolysis, we have to bear in mind that covalent compounds are poor electrical conductors, including pure water (see section 6.4). Therefore, in order to create an electron flow between the two electrodes, an ionic compound, such as the salt sodium sulfate (Na_2SO_4) or sodium nitrate ($NaNO_3$), is usually added to the water since they easily ionize in aqueous solutions and conduct electricity (see section 6.3).

Given that water can be both oxidized and reduced, we obtain the following half-equations as well as the net reaction for the **electrolysis of water**:

$$\begin{cases} \text{Cathode:} & 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) \\ \text{Anode:} & 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \\ \text{Net reaction:} & 2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g) \end{cases} \tag{12.14}$$

In an electrolytic solution of, let's say, sodium sulfate (Na_2SO_4), the sodium cations (Na^+) are attracted towards the cathode (–), so that aqueous sodium hydroxide (NaOH) is formed. In a similar fashion, a solution of sulphuric acid (H_2SO_4) forms around the anode (+).

By mixing the anodic and cathodic solutions, the original sodium sulfate (Na_2SO_4) solution can be regenerated (see Equation 9.13), which means that water is the only substance being consumed in this electrolytic process.

12.4 Electroplating

Electrolytic cells are often put to use in a process called **electroplating**, which involves applying a thin coating of metal onto a conducting surface. The purpose of electroplating ranges from protection against corrosion and aesthetics to the strengthening of a surface and the purification of metals. Examples include silver-plated cutlery, galvanized steel, chrome-plated bathroom fittings and automobile parts, and gold-plated jewelry.

The object that needs a coated layer serves as the *cathode* in the electrolytic cell, because the metal that will serve as the coating must be reduced to eventually become deposited onto the object.

Let us consider the example whereby we wish to adorn a key with a layer of silver. A possible configuration of the cell is a piece of silver (Ag) acting as the anode, an old key as the cathode, and silver nitrate ($AgNO_3$) as the electrolytic solution. This gives the following possible half-reactions:

$$\begin{array}{ll} \textit{Cathode} & \begin{cases} Ag^+(aq) + e^- \longrightarrow Ag(s) & (E^\circ = 0.80) \\ 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq) & (E^\circ = -0.83) \end{cases} \\ \\ \textit{Anode} & \begin{cases} Ag(s) \longrightarrow Ag^+(aq) + e^- & (E^\circ = 0.80) \\ 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- & (E^\circ = 1.4) \end{cases} \end{array} \tag{12.15}$$

Note that this electrolytic process makes uses of an **active electrode**, i.e., the silver anode, which means that the metal of which the anode is made participates in the electrolysis, unlike all the previous examples in this chapter (except for the example discussed in Fig. 12.1).

The above half-reactions imply that the cathode is reducing silver cations (Ag^+), which originate both from the solution as well as from the anode, and thereby providing the key with a fresh layer of silver.

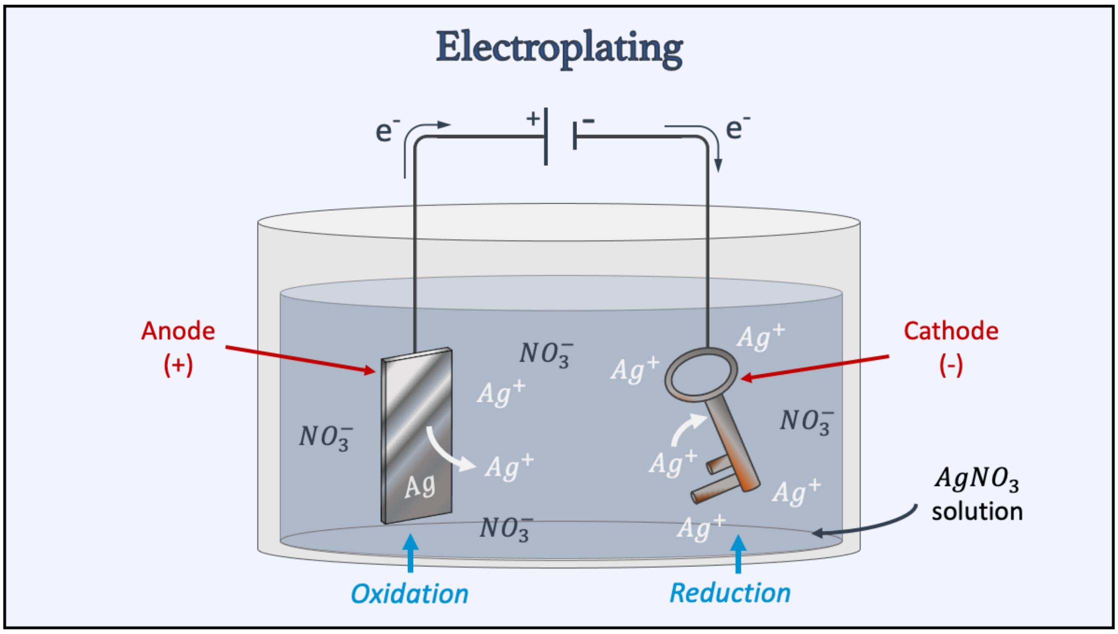


Figure 12.4: The technique of electroplating

13 Carbon Chemistry

13.1 General Concepts

13.1.1 A Definition

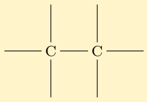
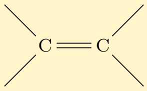
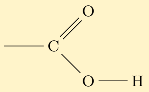
In a nutshell, carbon or organic chemistry is the academic discipline within the field of chemistry that studies the features and reactions of carbon-containing compounds, i.e., the so-called **organic compounds**. One of those compounds include **hydrocarbons**, whose individual components exist exclusively of the elements carbon (C) and hydrogen (H). Examples of hydrocarbons are methane (CH_4), ethene (C_2H_4), and benzene (C_6H_6). These particular carbon-based compounds are formed as the result of the slow maturation of hydrogen-rich, oxygen-poor ancient organic matter (biomass) buried deep within sediments.

The natural sources of hydrocarbons are commonly referred to as **fossil fuels** and include crude oil and natural gas. **Crude oil**, one of the major sources of hydrocarbons, consists of a liquid mixture of various hydrocarbon groups called *fractions*, of which alkanes form the largest fraction (see section 13.2). In order for crude oil to be usable in our industrialized society, it must be refined, which implies that the fractions are physically separated from one another by the method of *fractional distillation* (see section 8.2).

13.1.2 Functional Groups

Organic compounds are subdivided into several families called **homologous series** according to the type of **functional group** that the compounds carry with them—a functional group is a group of atoms that represents the *reactive part* of the compound. Among the many homologous series, we discuss four of them in this chapter, i.e., alkanes and alkenes (section 13.2), alcohols (section 13.4), and carboxylic acids (section 13.5).

Table 13.1: The functional groups

Homologous Series	**Functional Group**	**Functional Group Name**
Alkanes		Carbon single bond
Alkenes		Carbon double bound
Alcohols	$—O—H$	Hydroxyl group
Carboxylic acids		Carboxyl group

When a functional group that contains elements other than carbon (C) or hydrogen (H) is added to a hydrocarbon, the compound is designated as a **hydrocarbon derivative**. As a case in point, the alkanes and alkenes are classified as hydrocarbons—they are composed of hydrogen (H) and carbon (C) atoms only—while the homologous series alcohols and carboxylic acids are considered hydrocarbon derivatives, given that the functional groups -OH (the hydroxyl group) and -COOH (the carboxyl group) are added, respectively.

13.1.3 Structure and Naming

Another feature that sets the various homologous series apart from one another is the fact that every series is characterized by a **general formula**, which describes the *molecular formula* of the individual compounds. The general formulae of the four homologous series under discussion are C_nH_{2n+2} (alkanes), C_nH_{2n} (alkenes), $C_nH_{2n+1}OH$ (alcohols), and $C_nH_{2n+1}COOH$ (carboxylic acids), whereby we will mostly limit ourselves to the first six compounds of every series, i.e., $n \in \{1, \cdots, 6\}$ (for the alkanes, alkenes, and alcohols) and $n \in \{0, \cdots, 5\}$ (for the carboxylic acids).

In terms of the structural notation of the organic compounds, a distinction is made between the concepts molecular formula, condensed structural formula, and full structural (displayed) formula. The **molecular formula** points out the number of individual elements that are present in the compound without revealing any information about how they form bonds. For instance, the molecular formula of the alkane pentane is C_5H_{12}. The **condensed structural formula** discloses the type of bonds and the order in which the atoms are connected without graphically representing it. For example, the condensed structural formula of the alkene hex-1-ene is $CH_2{=}CH(CH_2)_3CH_3$. The **full structural (displayed) formula** shows in a visual manner how the individual atoms connect together. In the case of the carboxylic acid butanoic acid (C_3H_7COOH), its full structural formula is the following:

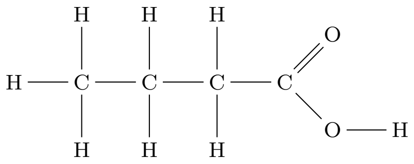


Figure 13.1: The full structural (displayed) formula of butanoic acid

Moreover, hydrocarbons come in different shapes, such as **linear straight-chain** compounds, **branched** compounds, and **cyclic** compounds. In this chapter, we will focus only on the straight-chain hydrocarbons. An example is depicted in Fig. 13.1.

Concerning the **nomenclature** of hydrocarbons, the *base segment or the root* of the name indicates the number of carbon (C) atoms present in the (parent) chain (see Table 13.2 below), while the *suffix* reveals the type of functional group attached to the chain. For the four homologous series under consideration, the suffices are -*ane* (alkanes), -*ene* (alkenes), -*anol* (alcohols), and -*anoic acid* (carboxylic acids).

For instance, the base segment *eth-* of the compound ethanol (C_2H_5OH) reflects the presence of *two* carbon (C) atoms, and the suffix -*anol* reveals that we are dealing with an alcohol. Table 13.2 provides an overview of the base segments for the first six carbon (C) atoms together with a couple of examples of individual compounds of our four homologous series.

Table 13.2: The basic nomenclature of organic compounds

# Carbon Atoms	Base Segment	Example of Suffix	Homologous Series	Full Name	Molecular Formula
1	***meth-***	-anol	alcohols	methanol	CH_3OH
2	***eth-***	-anoic acid	carboxylic acids	ethanoic acid	CH_3COOH
3	***prop-***	-ane	alkanes	propane	C_3H_8
4	***but-***	-ene	alkenes	butene	C_4H_8
5	***pent-***	-anol	alcohols	pentanol	$C_5H_{11}OH$
6	***hex-***	-anoic acid	carboxylic acids	hexanoic acid	$C_5H_{11}COOH$

In fact, the **International Union of Pure and Applied Chemistry (IUPAC)** has designed specific rules for chemical nomenclature, and we will apply them to the four homologous series under discussion. When it comes to the **alkanes**, the names for the first six compounds are methane, ethane, propane, butane, pentane, and hexane, since we only consider linear straight-chain hydrocarbons and there are only single carbon (C) bonds present in the chain.

Regarding the **alkenes**, the hydrocarbon compound can feature one or more double bonds, so that the Greek numerical prefixes *di-*, *tri-*, *tetra-*, and *penta-* reflect the *number* of double bonds, i.e., 2, 3, 4, and 5, respectively. The suffix *-ene* absorbs these prefixes and takes on the form *-adiene*, *-atriene*, *-atetraene*, and *-apentaene*, respectively. In terms of the *position* of the double bond(s), the Arabic numerals 1,2,3,4, and 5 represent the respective position and are inserted in the suffix between the letter *a* and the numerical prefix. In case of just one double bond, the number 1 is placed right in front of the suffix *-ene*. Bear in mind that you start counting at that side of the carbon chain making sure that the value of the position remains as small as possible.

For example, the compound $CH_2{=}C{=}CH_2$ is named propa-1,2-diene. The base segment is *prop-*, as there are three carbon (C) atoms, and given two double bonds, we make use of the suffix *-adiene*. The two double bonds come in position number 1 and 2, so that we adapt the suffix to *-a-1,2-diene*. Another example is the compound $CH_2{=}CHCH_2CH_3$. As there are four carbon (C) atoms and only one double bond, which is located at the first position (not the fourth, because $1 < 4$), the name of the hydrocarbon is but-1-ene. A third example is the compound $CH_2{=}C{=}CHCH_2CH{=}C$. With six carbon (C) atoms and three double bonds in position 1, 2, and 5 (not 1, 4, and 5, because $2 < 4$), the name becomes hexa-1,2,5-triene.

Note that sometimes the number of the positions are written in front of the *base segment*, so that the above examples become 1,2-propadiene, 1-butene, and 1,2,5-hexatriene. In this chapter, we will stick to the original (preferred) IUPAC formulation.

Concerning the **alcohols**, more than one hydroxyl group (-OH) can be introduced into the carbon chain, so that the general format of the name becomes *(name of the respective alkane)-(the position(s) of the hydroxyl group)-(the corresponding numerical prefix followed by -ol)*. If there are four hydroxyl groups, the suffix *-tetraol* is shortened to *-tetrol*. Keep furthermore in mind that the alkane name loses its final letter *e* in case of just one hydroxyl group.

For instance, the compound $CH_3CH(OH)CH_2OH$ is called propane-1,2-diol, while the compound $CH_3CH(OH)CH_3$ is referred to as propan-2-ol. Given that in the latter case there is only one hydroxyl group, the name of the associated alkane loses its final letter *e*. Some other examples of alcohols are $(CH_2OH)_2$ (ethane-1,2-diol), $CH_3C(OH)_2CH_3$ (propane-2,2-diol), $CH_2(OH)CH_2CH(OH)CH_2OH$ (butane-1,2,4-triol), $CH_2(OH)CH_2(CH(OH))_2CH_2OH$ (pentane-1,2,3,5-tetrol), and $CH_3(CH(OH))_4CH_2OH$ (hexane-1,2,3,4,5-pentaol). The full structural formula of pentane-1,2,3,5-tetrol is the following:

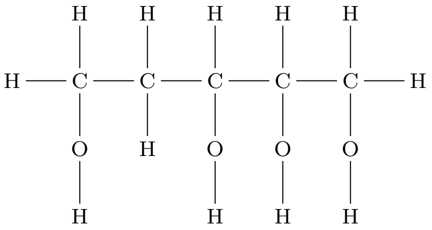


Figure 13.2: The full structural (displayed) formula of pentane-1,2,3,5-tetrol

If alcohols contain double bonds, the naming rules of both the alkenes and the alcohols are combined, so that the generic format of the name is slightly altered to *(name of the respective alkene)-(the position(s) of the hydroxyl group)-(the corresponding numerical prefix followed by -ol)*. Bear in mind that the side of the carbon chain at which you start counting the positions is determined by the *hydroxyl group*.

For example, the compound $CH_2{=}CHCH_2OH$ is called prop-2-en-1-ol (and not prop-1-en-3-ol), the compound $CH_2{=}C(OH)CH_3$ is designated as prop-1-en-2-ol, and the compound $CH_2{=}C(OH)CHOH$ is referred to as prop-2-ene-1,2-diol. Other examples include the compounds $CH_3C(OH){=}C{=}CH_2$ (buta-2,3-dien-2-ol), $CH_2(OH)CH(OH)C(OH){=}CH_2$ (but-3-ene-1,2,3-triol), $CH_2{=}C(OH)(CH(OH))_2CH_2OH$ (pent-4-ene-1,2,3,4-tetrol), and, lastly, the compound $CH_2{=}CHC(OH){=}C(OH)CH{=}CH_2$ (hexa-1,3,5-triene-3,4-diol), which has the following full structural formula:

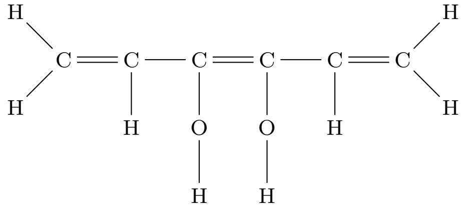


Figure 13.3: The full structural (displayed) formula of hexa-1,3,5-triene-3,4-diol

Finally, with regard to the **carboxylic acids**, the carboxyl group -COOH can only be placed at the endings of a carbon chain. If only one carboxyl group is present, the position number 1 is typically omitted from the name. In this case, the generic format of the name is *(name of the respective base segment followed by the suffix -anoic acid)*. However, if a carboxyl group is located both at the beginning and at the end of a chain, the general format of the name becomes *(name of the respective alkane followed by the adapted suffix -dioic acid)*. In case of *one* carboxyl group and the presence of one or more double bonds in the carbon chain, the general format reads as follows: *(name of the respective alkene followed by the suffix -oic acid)*. If the chain carries *two* carboxyl groups and has one or more double bonds, the general format is altered to *(name of the respective alkene followed by the suffix -dioic acid).* Keep in mind that the side of the carbon chain at which you start counting the positions is determined by the *carboxyl group.*

For instance, the compound CH_3CH_2COOH is named propanoic acid, the compound with two carboxyl groups $(HOOC)CH_2COOH$ is designated as propanedioic acid, and the compound $CH_2{=}CHCOOH$ is called prop-2-enoic acid. Further examples include the compound $CH_2{=}CHCH_2COOH$ (but-3-enoic acid), the compound $(HOOC)CH{=}CHCOOH$ (but-2-enedioic acid), the compound $(HOOC)CH{=}C{=}CHCH_3$ (penta-2,3-dienoic acid), the compound $(HOOC)CH{=}C{=}CHCOOH$ (penta-2,3-dienedioic acid), and, lastly, the compound $(HOOC)CH{=}(CH)_2{=}C{=}CH_3$ (hexa-2,4,5-trienoic acid). The full structural formula of but-2-enedioic acid looks as follows:

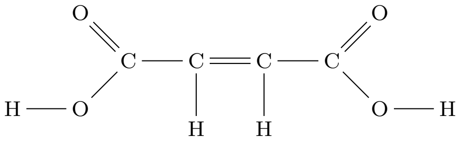
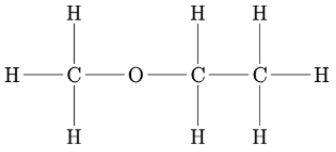


Figure 13.4: The full structural (displayed) formula of but-2-enedioic acid

A structural characteristic of organic compounds is **structural isomerism**, which refers to the situation whereby two or more compounds share the same *molecular formula* but differ in terms of *structural formula.* The *longer* the carbon chain, the *greater* the number of possible structural isomers. As a case in point, the hydrocarbon C_4H_{10} has two structural isomers, C_8H_{18} has eighteen, and $C_{10}H_{22}$ has seventy-five of them.

For example, the organic compound C_3H_8O has the following three structural isomers: propan-1-ol, propan-2-ol, and ethyl-methyl ether—an ether is another homologous series whereby two parts of a carbon chain are attached to an oxygen (O) atom. The corresponding full structural formulae look as follows:

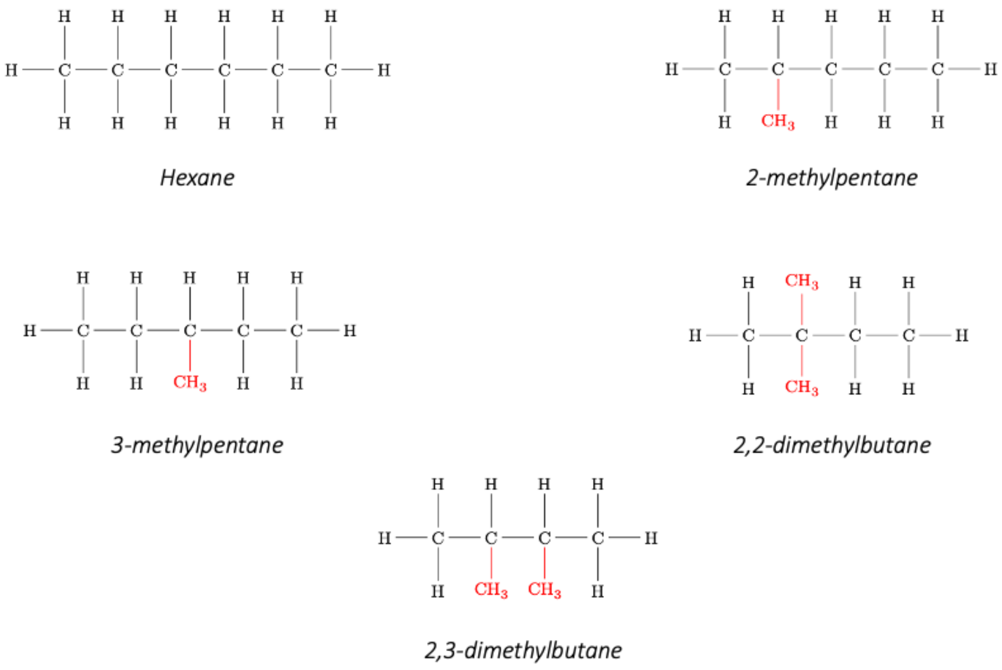
Propan-1-ol *Propan-2-ol*



Ethyl-methyl ether

Figure 13.5: The three structural isomers of C_3H_8O

Another example is the hydrocarbon C_6H_{14}, which converts into five structural isomers, i.e., hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane. Apart from hexane, the other four hydrocarbons are *branched* alkanes, which fall outside the scope of this preparation course. The respective full structural formulae are:



Hexane

2-methylpentane

3-methylpentane

2,2-dimethylbutane

2,3-dimethylbutane

Figure 13.6: The five structural isomers of C_6H_{14}

13.1.4 Chemical Properties

Every homologous series is characterized by **similar chemical properties** since all the compounds within a homologous series share the *same functional group*, which is the main site of chemical reactions. For example, when carboxylic acids react with alcohols, another homologous series is formed called esters (more on this in section 13.5). What is more, alcohols can oxidize into carboxylic acids, which is illustrated when wine is exposed to the open air for a longer period of time, i.e., it turns sour.

Another case is the **complete combustion** of the straight-chain organic compounds of the four homologous series under consideration. This chemical process (at 25°C) is represented by the following general chemical equations (keep in mind that $n \in \{1, \cdots, 6\}$ for the alkanes, alkenes, and alcohols and $n \in \{0, \cdots, 5\}$ for the carboxylic acids):

$$\begin{cases} \text{Alkanes:} & 2\,C_nH_{2n+2}(l \text{ or } g) & + & (3n+1)\,O_2(g) & \longrightarrow & 2(n+1)\,H_2O(g) & + & 2n\,CO_2(g) \\ \text{Alkenes:} & 2\,C_nH_{2n}(l \text{ or } g) & + & 3n\,O_2(g) & \longrightarrow & 2n\,H_2O(g) & + & 2n\,CO_2(g) \\ \text{Alcohols:} & 2\,C_nH_{2n+1}OH(l) & + & 3n\,O_2(g) & \longrightarrow & 2(n+1)\,H_2O(g) & + & 2n\,CO_2(g) \\ \text{Carboxylic acids:} & 2\,C_nH_{2n+1}COOH(l) & + & (3n+1)\,O_2(g) & \longrightarrow & 2(n+1)\,H_2O(g) & + & 2(n+1)\,CO_2(g) \end{cases} \tag{13.1}$$

For instance, the complete combustion of methane (CH_4), ethene ($CH_2{=}CH_2$), propan-1-ol ($CH_3(CH_2)_2OH$), and pentanoic acid ($CH_3(CH_2)_3COOH$) reflected by the following chemical equations, respectively (at 25°C):

$$\left\{\begin{array}{llcllcllcl}
\text{Methane:} & \mathrm{CH_4}(g) & + & 2\,\mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{H_2O}(g) & + & \mathrm{CO_2}(g) \\
\text{Ethene:} & \mathrm{C_2H_4}(g) & + & 3\,\mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{H_2O}(g) & + & 2\,\mathrm{CO_2}(g) \\
\text{Propan-1-ol:} & 2\,\mathrm{C_3H_7OH}(l) & + & 9\,\mathrm{O_2}(g) & \longrightarrow & 8\,\mathrm{H_2O}(g) & + & 6\,\mathrm{CO_2}(g) \\
\text{Pentanoic acid:} & 2\,\mathrm{C_4H_9COOH}(l) & + & 13\,\mathrm{O_2}(g) & \longrightarrow & 10\,\mathrm{H_2O}(g) & + & 10\,\mathrm{CO_2}(g)
\end{array}\right. \tag{13.2}$$

However, if there is an insufficient amount of oxygen present, the chemical reaction will be that of an **incomplete combustion**, whereby carbon (C) and carbon monoxide (CO) can form. In terms of physical characteristics, complete combustion is accompanied by a blue flame, whereas incomplete combustion typically produces a yellow flame as well as smoke, whose constituents are microscopic carbon (C) particles which are eventually deposited as soot. A couple of examples of equations of incomplete combustion are the following (at 25°C):

$$\left\{\begin{array}{llclclclcl}
\text{Propane:} & \mathrm{C_3H_8}(g) & + & 3\,\mathrm{O_2}(g) & \longrightarrow & \mathrm{C}(s) & + & 2\,\mathrm{CO}(g) & + & 4\,\mathrm{H_2O}(g) \\
\text{Buta-1,2-diene:} & \mathrm{C_4H_8}(g) & + & 4\,\mathrm{O_2}(g) & \longrightarrow & & & 4\,\mathrm{CO}(g) & + & 4\,\mathrm{H_2O}(g) \\
\text{Ethanol:} & \mathrm{C_2H_5OH}(l) & + & \mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{C}(s) & & & + & 3\,\mathrm{H_2O}(g) \\
\text{Hexanoic acid:} & \mathrm{C_5H_{11}COOH}(l) & + & 5\,\mathrm{O_2}(g) & \longrightarrow & & & 6\,\mathrm{CO}(g) & + & 6\,\mathrm{H_2O}(g)
\end{array}\right. \tag{13.3}$$

13.1.5 Physical Properties

Within each homologous series, a distinct trend appears in terms of various **physical properties**. Regarding their **boiling points**, the *higher* the number of carbon (C) atoms that the individual compound possesses (which results in a higher carbon chain length), the *stronger* the inter-molecular London dispersion forces (see section 6.6), and thus the *higher* the temperature at which it progresses from a liquid into a gaseous phase. Put differently, compounds with a shorter chain length are more volatile, i.e., they evaporate more easily.

When we compare the boiling points *between* the series, the alcohols and carboxylic acids show *higher* boiling points in comparison with the alkanes and alkenes due to the presence of the dipole-dipole interactions as well as hydrogen bonding in addition to the weak van der Waals forces. Table 13.3 lists some examples for each of the four homologous series under discussion:

Table 13.3: The boiling point of some organic compounds

Name Compound	Molecular Formula	Boiling Point (in °C)	Homologous Series
Methane	CH_4	-161.5	Alkane
Propane	C_3H_8	-42.1	Alkane
Pentane	C_5H_{12}	36.0	Alkane
Ethene	C_2H_4	-103.7	Alkene
But-1-ene	C_4H_8	-6.2	Alkene
Hex-1-ene	C_6H_{12}	63.4	Alkene
Methanol	CH_3OH	64.7	Alcohol
Propan-1-ol	C_3H_7OH	97.2	Alcohol
Pentan-1-ol	$C_5H_{11}OH$	137.9	Alcohol
Ethanoic acid	CH_3COOH	117.9	Carboxylic acid
Butanoic acid	C_3H_7COOH	163.7	Carboxylic acid
Hexanoic acid	$C_5H_{11}COOH$	205.2	Carboxylic acid

As a result of these inter-molecular forces, another physical property called **viscosity**—this is the tendency of a fluid to resist its flow—equally *increases* as the carbon chain of the compound *grows* within each homologous series. In other words, longer carbon chains are thicker (more viscous).

Finally, in terms of **flammability**, we observe a *reversed* trend. That is, the *larger* the number of carbon (C) atoms, the *higher* the number of covalent bonds to break upon combustion, and thus the *weaker* the flammability of the respective compound. Stated another way, the *smaller* a compound, the *more volatile* and therefore the *more flammable* it is, since it is the *vapour* above the liquid, rather than the liquid itself, that burns.

13.2 Alkanes and Alkenes

The **alkanes** (C_nH_{2n+2}) are referred to as **saturated hydrocarbons**, given that they do not tend to react with other compounds due to the presence of only *single bonds*—in that sense, the alkanes do not really have a functional group (see Table 13.1). In contrast, the **alkenes** (C_nH_{2n}) are called **unsaturated hydrocarbons** as a result of the presence of *double bonds*, which can be broken, so that the alkenes can interact with other compounds.

When large hydrocarbon chains (crude oil) go through the process of fractional distillation (see section 8.2), some of the separated fractions are still too large and thus not particularly valuable for further industrial processing. In order to be useful, they must be further split into smaller carbon chains, i.e., a process called **cracking**, so that they can burn more easily and become economically beneficial—remember that hydrocarbons ignite more rapidly with a declining chain length (see section 13.1.5). Cracking occurs either under high temperatures (*thermal or steam cracking*) or with the assistance of a catalyst (*catalytic cracking*), or a combination of both methods.

When partitioning the initially long alkane chain, the generated products exist of either shorter alkane and alkene chains or shorter alkene chains and hydrogen gas (H_2). The saturated alkane products typically find an economic purpose as *fuel*, whereas the unsaturated alkene products are generally used for the *manufacturing of polymers* (see section 13.3).

A first example is the cracking of the hydrocarbon $C_{15}H_{32}$ (pentadecane), which could result in the following chemical equations:

$$\begin{cases} \underset{\text{(pentadecane)}}{C_{15}H_{32}(g)} \longrightarrow \underset{\text{(hexane)}}{C_6H_{14}(g)} + \underset{\text{(prop-1-ene)}}{3\,C_3H_6(g)} \\[2ex] \underset{\text{(pentadecane)}}{C_{15}H_{32}(g)} \longrightarrow \underset{\text{(oct-3-ene)}}{C_8H_{16}(g)} + \underset{\text{(but-1-ene)}}{C_4H_8(g)} + \underset{\text{(prop-1-ene)}}{C_3H_6(g)} + \underset{\text{(hydrogen gas)}}{H_2(g)} \\[2ex] \underset{\text{(pentadecane)}}{C_{15}H_{32}(g)} \longrightarrow \underset{\text{(octane)}}{C_8H_{18}(g)} + \underset{\text{(prop-1-ene)}}{C_3H_6(g)} + \underset{\text{(ethene)}}{2\,C_2H_4(g)} \end{cases} \tag{13.4}$$

As a result of the balancing of equations (conservation of mass), one can identify a missing product. For instance, if hexane (C_6H_{14}) is being cracked and we know that ethene (C_2H_4) is one of the two generated products, then we can find the missing product by balancing the equations, i.e., the second product must contain $6 - 2 = 4$ carbon (C) and $14 - 4 = 10$ hydrogen (H) atoms. Two possible outcomes are the following:

$$\begin{cases} \underset{\text{(hexane)}}{C_6H_{14}(g)} \longrightarrow \underset{\text{(butane)}}{C_4H_{10}(g)} + \underset{\text{(ethene)}}{C_2H_4(g)} \\[2ex] \underset{\text{(hexane)}}{C_6H_{14}(g)} \longrightarrow \underset{\text{(ethane)}}{2\,C_2H_5(g)} + \underset{\text{(ethene)}}{C_2H_4(g)} \end{cases} \tag{13.5}$$

A third example is the cracking of the hydrocarbon $C_{20}H_{42}$ (eicosane), which may yield the following products:

$$\begin{cases} \underset{\text{(eicosane)}}{C_{20}H_{42}(g)} \longrightarrow \underset{\text{(octane)}}{C_8H_{18}(g)} + \underset{\text{(hexa-1,3-diene)}}{C_6H_{10}(g)} + \underset{\text{(butane)}}{C_4H_{10}(g)} + \underset{\text{(ethene)}}{C_2H_4(g)} \\[2ex] \underset{\text{(eicosane)}}{C_{20}H_{42}(g)} \longrightarrow \underset{\text{(octane)}}{C_8H_{18}(g)} + \underset{\text{(hex-3-ene)}}{C_6H_{12}(g)} + \underset{\text{(but-2-ene)}}{C_4H_8(g)} + \underset{\text{(ethene)}}{C_2H_4(g)} \\[2ex] \underset{\text{(eicosane)}}{C_{20}H_{42}(g)} \longrightarrow \underset{\text{(nonane)}}{C_9H_{20}(g)} + \underset{\text{(pent-2-ene)}}{C_5H_{10}(g)} + \underset{\text{(prop-1-ene)}}{2\,C_3H_6(g)} \end{cases} \tag{13.6}$$

Due to the unsaturated nature of alkenes, they interact with other compounds, upon which the double bonds are broken. In case they interact with hydrogen (H_2), halogens (Group 17), hydrogen halides (e.g., HF), or steam (H_2O), the chemical reactions are referred to as **addition reactions**. When reacting with hydrogen, halogens, or hydrogen halides, the alkenes convert into *alkanes*, whereas reactions with steam produce *alcohols*. One feature that is shared among these reactions is the fact that the atoms of the interacting compound are added to the carbon (C) atoms that participate in the double bond(s).

The addition of **hydrogen (H_2)** is called *hydrogenation*, and an example is the hydrogenation of prop-1-ene (C_3H_6), which produces propane (C_3H_8):

$$C_3H_6(g) + H_2(g) \longrightarrow C_3H_8(g) \tag{13.7}$$

A more detailed schematic of the hydrogenation of prop-1-ene is provided below:

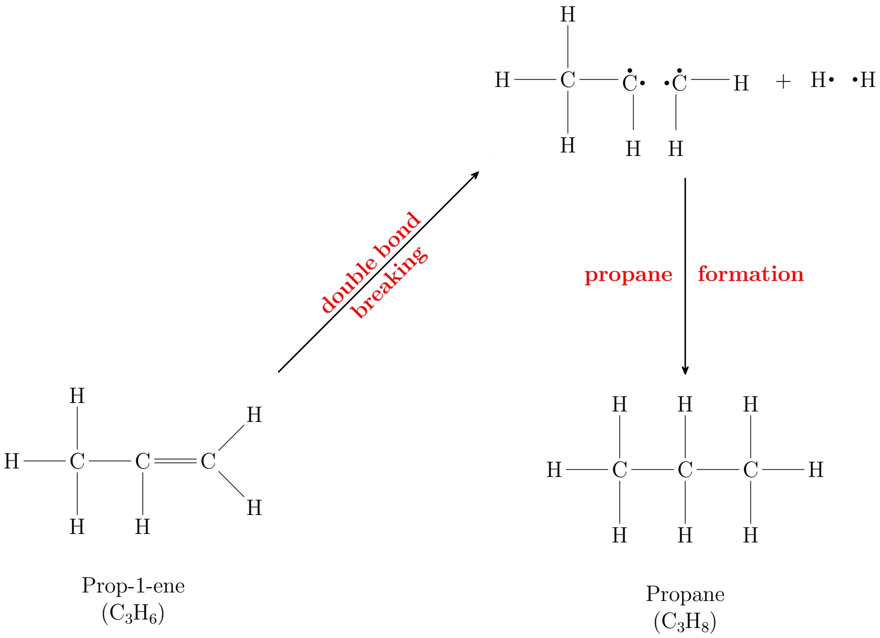
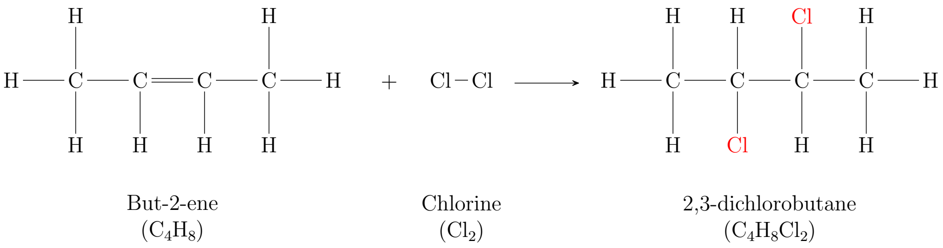


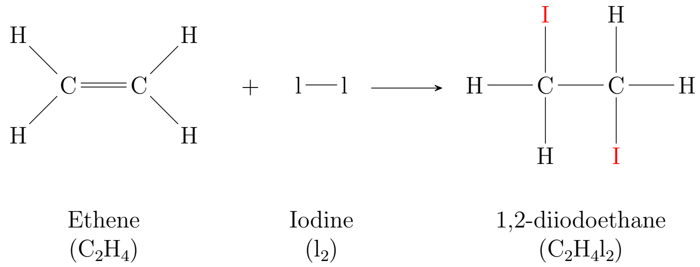
Figure 13.7: The hydrogenation of prop-1-ene (C_3H_6)

In the context of **halogens**, an example is the addition of chlorine gas (Cl_2) to the compound but-2-ene (C_4H_8), which produces the alkane 2,3-dichlorobutane ($C_4H_8Cl_2$):



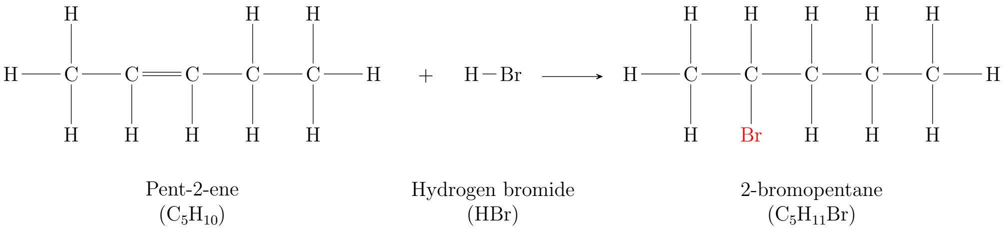
(13.8)

Given that the reactivity of the halogens *decreases* down the Group 17 (see section 7.2), the reaction 13.8 with chlorine (Cl_2) replaced by bromine (Br_2) would occur at a *slower* pace, and even slower still with iodine (I_2). Another example is the addition reaction (at 25°C) between ethene gas (C_2H_4) and the solid iodine (I_2), which gives the solid 1,2-diiodoethane ($C_2H_4I_2$):



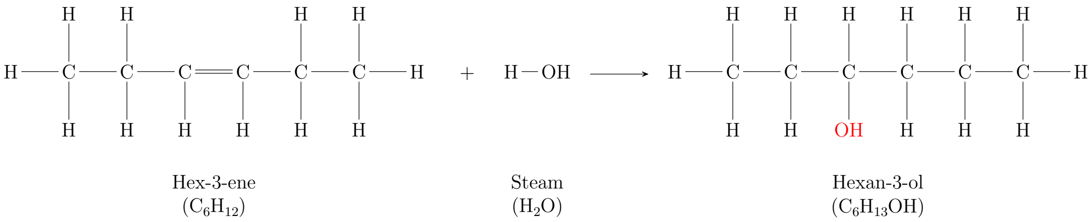
(13.9)

Regarding the addition of **hydrogen halides**, an example is the reaction (at 25°C) between the liquid pent-2-ene (C_5H_{10}) and hydrogen bromide gas (HBr), resulting in the liquid alkane 2-bromopentane ($C_5H_{11}Br$):



(13.10)

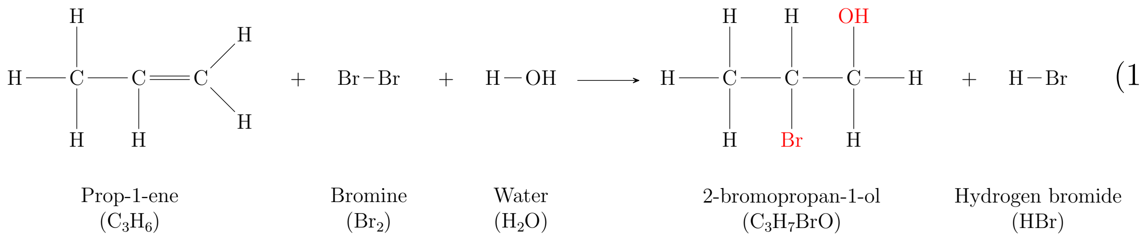
Lastly, an example of an addition reaction that involves **steam (H_2O)** is the reaction (at 25°C) between the liquid hex-3-ene (C_6H_{12}) and steam, which leads to the formation of the liquid *alcohol*—remember that addition reactions with steam produce alcohols, not alkanes—hexan-3-ol ($C_6H_{13}OH$):



(13.11)

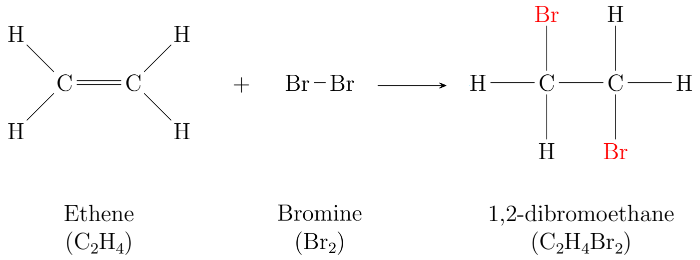
To find out whether a particular substance contains unsaturated hydrocarbons (alkenes), there exists a specific **test**, whereby the substance is mixed together with **bromine water**, which exhibits a *red-brownish colour.* If alkenes are present, the mixture immediately *loses* its colour (due to the reactivity of alkenes), whereas nothing much would happen if the substance only consisted of alkanes.

For instance, when the alkene prop-1-ene (C_3H_6) is mixed with bromine water, the major product formed is 2-bromopropan-1-ol (C_3H_7Br) together with hydrogen bromide (HBr):



(13.12)

However, when pure bromine (Br_2) is used instead—it is a liquid at 25°C—we obtain the following equation (this time with ethene (C_2H_4) as the reactant alkene):



(13.13)

13.3 Polymers

Organic compounds can engage in *addition reactions* with each other to form repetitive long-chain *saturated* compounds called **polymers**. The individual reactant compounds are referred to as **monomers**, and the addition process of monomers is known as **polymerization**.

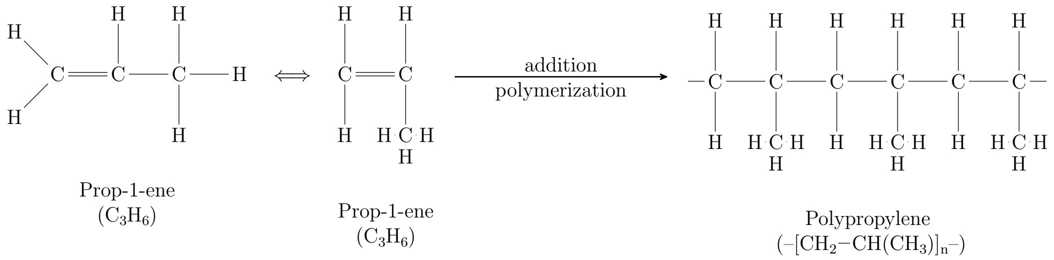
Generally, if the monomer contains a carbon double bond, i.e., the monomer is *unsaturated*, the polymerization process is designated as **addition polymerization**. In contrast, if one or more monomers without a carbon double bond contain a functional group at both of their endings, then the polymerization process is usually referred to as **condensation polymerization**.

The idiosyncratic feature of a polymer is its **repeat unit**, i.e., the repetitive molecular structure that forms the constitutive component of the polymer. In the context of *additional polymerization*, the repeat unit is equal to the (sum of the) monomer(s), whereas in the case of *condensation polymerization* the repeat unit is slightly different than the (sum of the) monomer(s), since a small covalent compound, e.g., water (H_2O) or hydrogen chloride (HCl), is typically expelled during the polymerization process.

13.3.1 Addition Polymerization

The distinctive characteristic of a polymer synthesized by addition polymerization is its backbone, which is a *continuous chain of carbon (C) atoms*. What happens during addition polymerization is the transformation of the carbon double bond into a single bond, and only the carbon (C) atoms that participated in the original double bond form part of the polymer backbone. In other words, any other carbon (C) or other atoms become branches of the polymer backbone, attached to the respective carbon (C) atom of the initial double bond.

Let us consider the example of the polymer *polypropylene*, whose monomer is propylene, which is the common name for prop-1-ene ($CH_2{=}CHCH_3$). Polypropylene is formed by addition polymerization of prop-1-ene, which can be illustrated as follows:



(13.14)

Note that in Equation 13.14 the chemical equation is not balanced. The letter n should be introduced in front of the structural formula of prop-1-ene, given that the monomer is repeated n times within the polymer structure of polypropylene. Fig. 13.8 indicates the repeat unit of polypropylene as well as two alternative ways of writing its structural formula—in the formula at the right-hand side, the zig-zag line represents the polymer's backbone carbon chain whereby the carbon (C) and hydrogen (H) atoms are implicitly assumed and therefore not drawn.

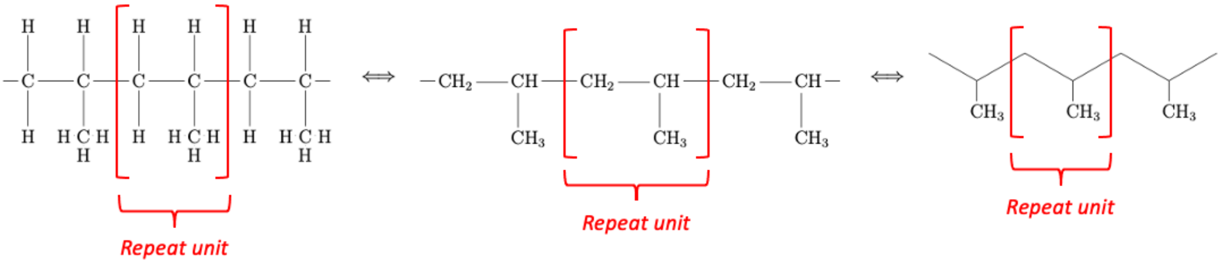


Figure 13.8: The repeat unit of the polymer polypropylene

In case of additional polymerization of just one monomer, the general structural formula of the respective polymer can be written as $-(repeat\ unit)_n-$, whereby the repeat unit equals the monomer with the double bond replaced by a single bond. Fig. 13.9 gives the example of the general formula of polypropylene.

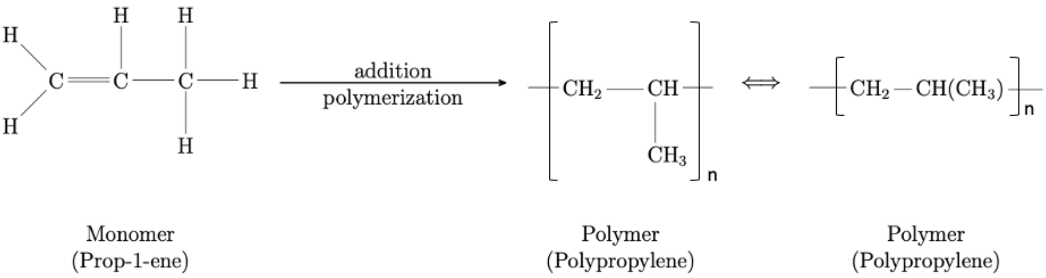


Figure 13.9: The general structural formula of the polymer polypropylene

Fig. 13.10 provides four additional examples, showing how the structural formula of the polymer is constructed based on the structural formula of the monomer. Conversely, Fig. 13.10 can also be used to derive the structural formula of the monomer when the general formula of the polymer is given—in this case, the single bond between the two carbon (C) atoms along the backbone of the polymer is simply replaced by a carbon double bond.

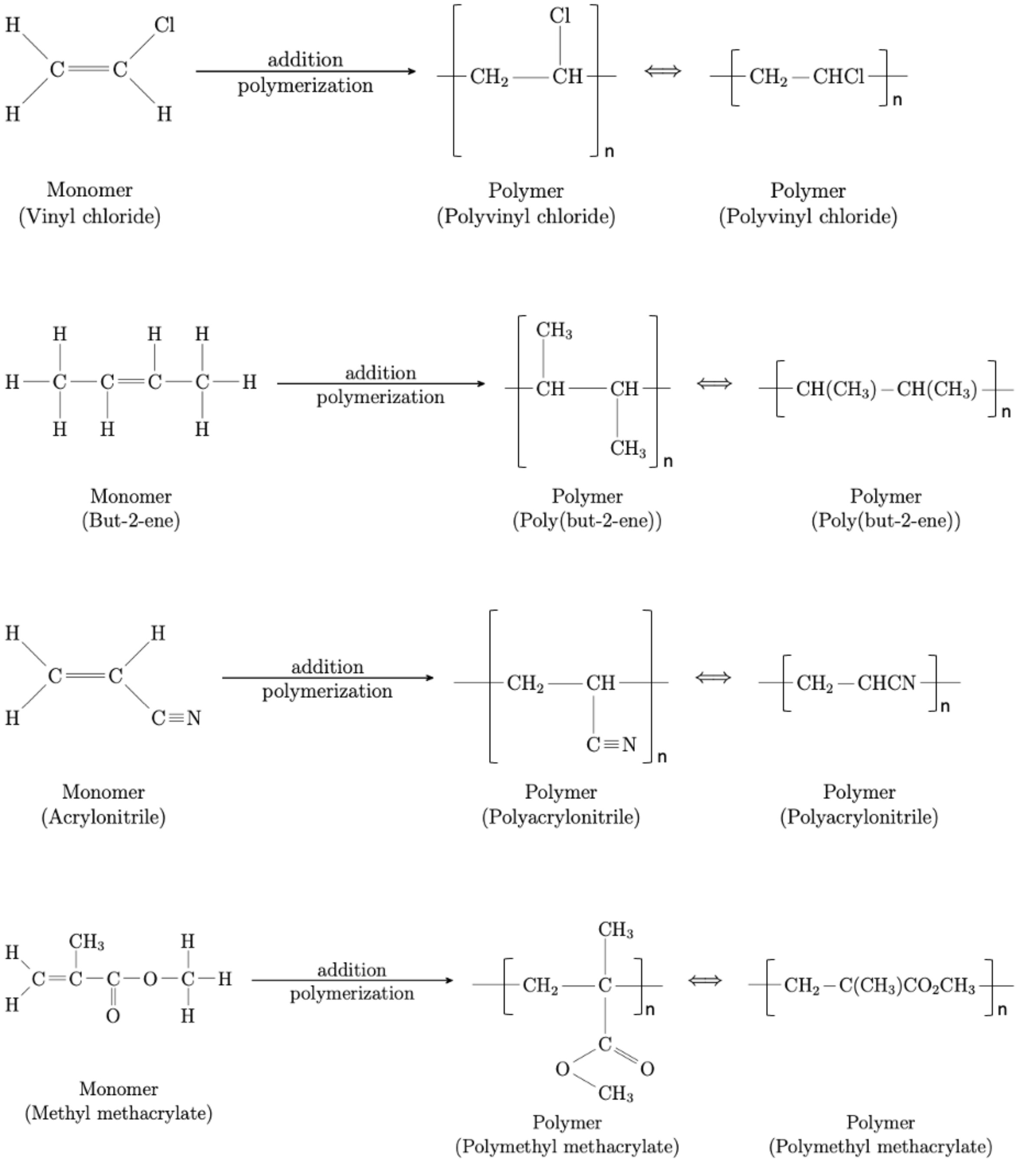


Figure 13.10: The general structural formula of some polymers

What is more, it is also possible to derive the general structural formula of a polymer starting from the displayed structure of the polymer chain. What we first need to do here is to correctly identify the *repeat unit* in the displayed schematic. Fig. 13.11 illustrates how this works using four examples.

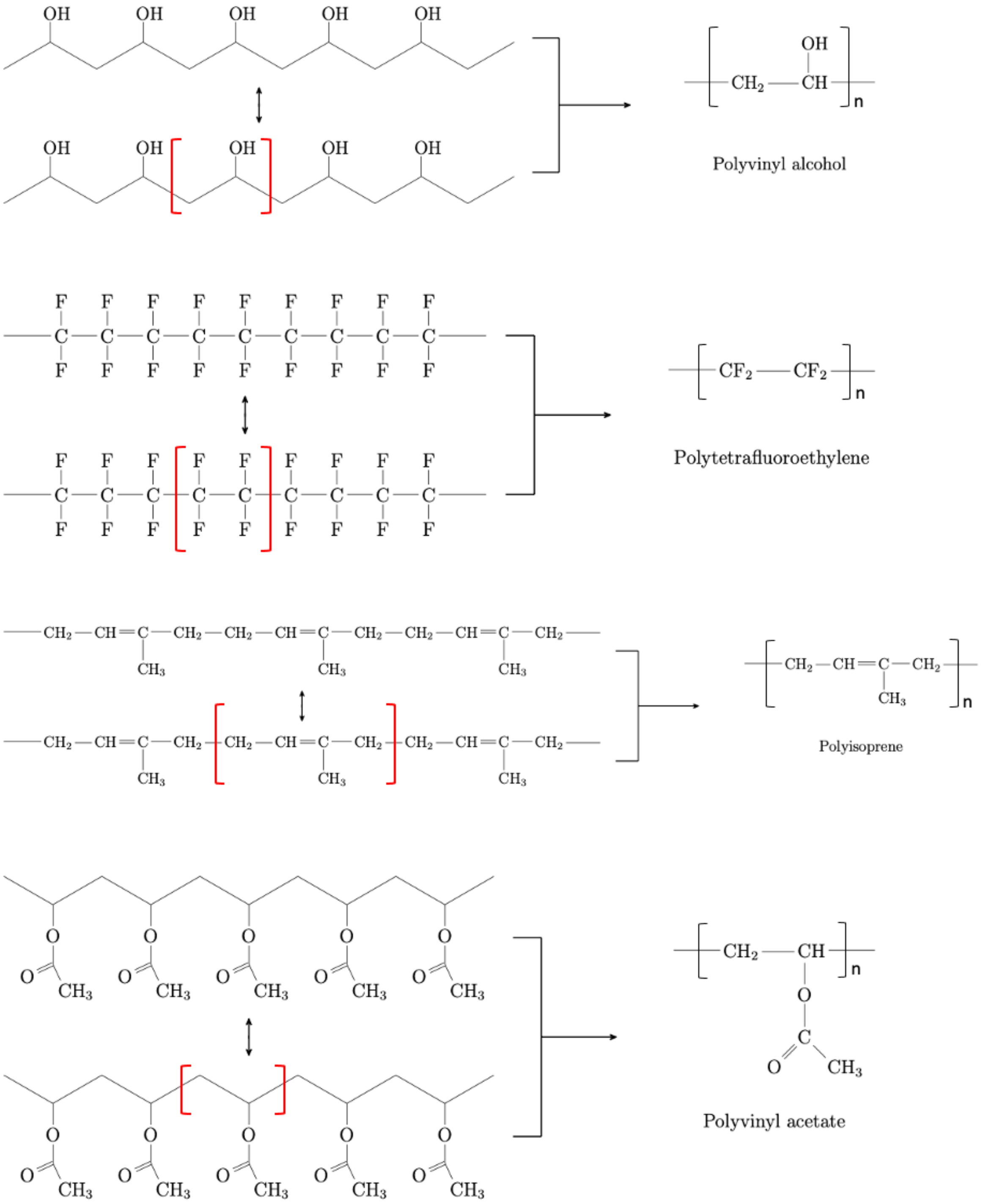


Figure 13.11: Identifying the general structural formula of some polymers

13.3.2 Condensation Polymerization

Unlike the polymers formed under addition polymerization, the backbone of the polymer synthesized via condensation polymerization also includes bonds between carbon (C) atoms and other atoms, such as oxygen (O) or nitrogen (N). In this section, we will focus on two types of condensation polymers: polyesters and polyamides.

Polyesters are polymers formed by creating *ester bonds*, whereby the functional group of esters (-COO) is born from the merger between a carboxyl group (-COOH) or the functional group -COCl and a hydroxyl group (-OH). Moreover, during their bonding process, a covalent compound of water (H_2O), or hydrogen chloride (HCl), is dislodged from the polymer chain.

A polyester polymer can be crafted by letting *identical* monomers react with each other, and whereby the monomers contain both a carboxyl group (or the group -COCl) and a hydroxyl group. What is more, a polyester can also be fashioned from the combination of two or more *different* monomers, whereby each monomer possesses either two identical or two different functional groups at their endings.

Polyamides are condensation polymers held together by *amide bonds*, which are characterized by the group -CONH and are the result of the unification between the amine group $-NH_2$ and the carboxyl group -COOH (or the functional group -COCl). Similar to polyesters, water (or hydrogen chloride) is ousted during polymerization, and the polymers are stitched together by combining unique monomers or several distinct monomers.

An **amino acid** is a monomer that contains both an amine group ($-NH_2$) and a carboxyl group (-COOH), and a condensation polymer made of several *different* amino acids is called a **peptide**. A **protein** is then defined as a long chain of peptides linked by amide bonds, a.k.a. *peptide bonds*—both peptides and proteins are thus polyamides.

In a first example, Fig. 13.12 demonstrates the reaction between three identical monomers commonly known as lactic acid, whereby each acid carries both a carboxyl group (-COOH) and a hydroxyl group (-OH). The result is the polyester polylactic acid, which in this example is made from three monomers.

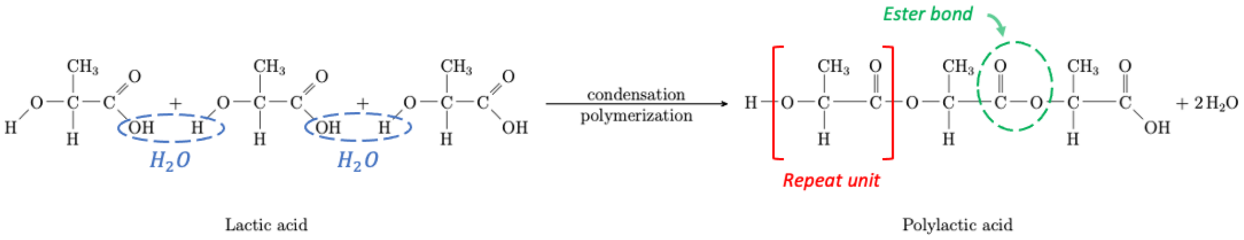


Figure 13.12: Condensation polymerization of lactic acid

In below Fig. 13.13, an example is shown of a polyester polymer that is the product of two distinct monomers, each carrying a hydroxyl (-OH) and a carboxyl group (-COOH).

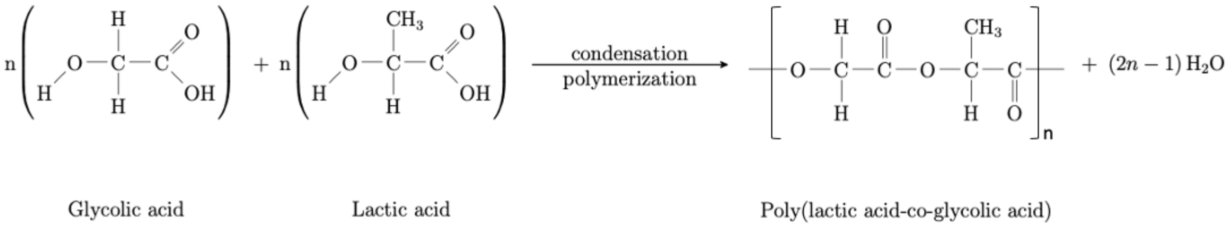


Figure 13.13: Condensation polymerization of lactic and glycolic acid

Next, Fig. 13.14 illustrates an example of the creation of a polyester as the result of condensation polymerization of two different monomers, whereby each monomer contains two identical functional groups, i.e., the group -COCl (pentanedioyl dichloride) and a hydroxyl group -OH (benzene-1,4-diol). Note that the hexagonal shape represents a benzene ring of carbon (C) atoms, which is not further discussed in this preparation course.

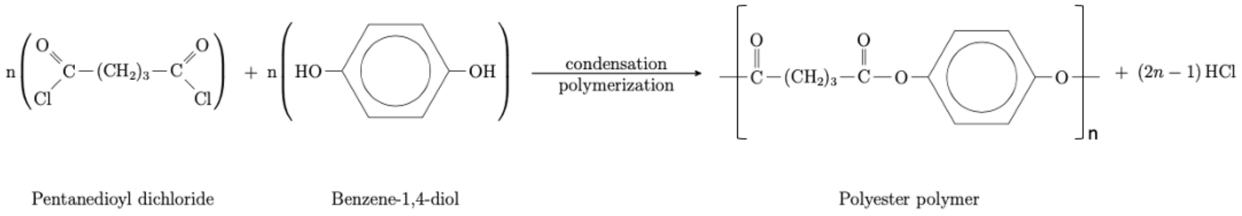


Figure 13.14: Two different monomers with two identical functional groups

When it comes to the polyamides, Fig. 13.15 outlines the formation of a peptide, whereby four amino acids, i.e., cysteine, alanine, aspartic acid, and threonine, are linked together through amide bonds (-CONH).

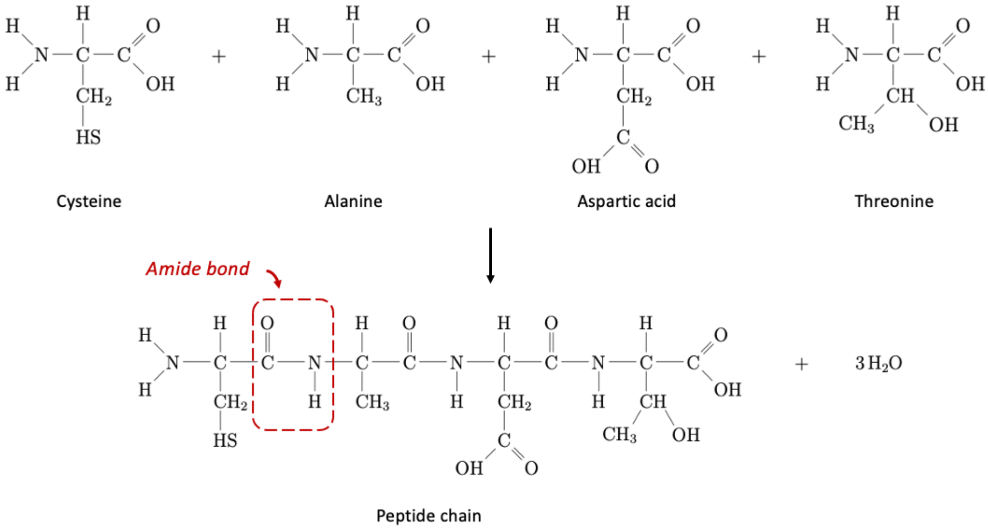


Figure 13.15: The formation of a peptide polymer

A classic example of a polyamide is presented in Fig. 13.16, which expresses the production of Nylon-6,6, whereby the amide bond emerges from the consolidation between an amine group (-NH_2) and the functional group -COCl.

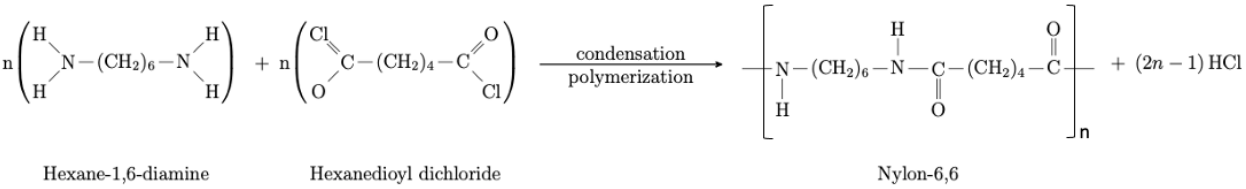


Figure 13.16: The production of Nylon-6,6

As a final example, Fig. 13.17 describes how a polyamide can also arise from the reaction between identical monomers, which contain two different functional groups, one of which being an amide group (-NH_2).

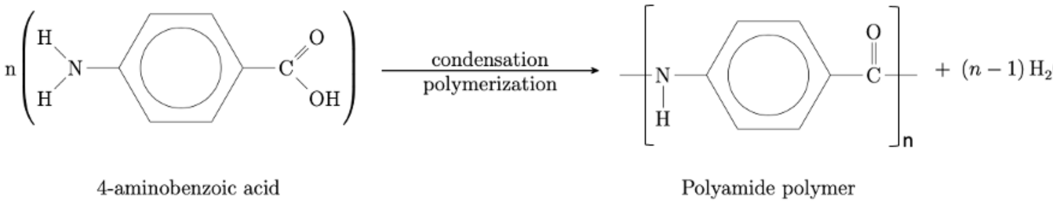


Figure 13.17: One monomer with two different functional groups

13.3.3 Biodegradability

Degradation is the process whereby a substance is decomposed into its original compounds or into newly assembled compounds. Some of the processes by which decomposition takes place include oxidation, hydrolysis (i.e., the addition of water breaks the chemical bond), photodegradation (i.e., the absorption of light that is subsequently accompanied by oxidation and hydrolysis), and degradation by enzymes (i.e., catalytic proteins) or microorganisms (i.e., bacteria, fungi, and algae).

Biodegradation refers to degradation by enzymes or microorganisms (which may rely on enzymatic oxidation or hydrolysis). Simply put, a substance is biodegradable if it spontaneously decomposes in a natural environment. Typically, physical degradation (e.g., oxidation, hydrolysis or photodegradation) constitutes the first step of degradation, after which biodegradation sets in. Microorganisms thereby break down the polymer fragments into even smaller parts and facilitate their transport to the enzymes within living cells, which, in turn, transform these fragments into polymer end products, such as adenosine triphosphate (ATP).

Regarding polymers, a distinction can be made between natural and synthetic polymers. **Natural polymers, a.k.a. agro-polymers or biopolymers,** are found in nature and are biodegradable. Examples include proteins (polypeptides) and polysaccharides (e.g., starch and cellulose). **Synthetic polymers** are created artificially mainly from petroleum-based products (crude oil), and most of these products are non-biodegradable. Some of these polymers include polyethylene, polypropylene (see Equation 13.14), polymethyl methacrylate (see Fig. 13.10), polyvinyl chloride, known as PVC (see Fig. 13.10), the polyester polyethylene terephthalate (PET), and the polyamide Nylon-6,6 (see Fig. 13.16).

The degree to which a polymer is biodegradable, i.e., the **biodegradability**, depends on a number of factors, such as the origin of the polymer (e.g., synthetic or natural), its chemical structure (e.g., the type of bonds), its chemical properties (e.g., solubility), and the environmental conditions in which degradation occurs (e.g., temperature and the presence of microorganisms).

Due to this wide range of influential factors, some synthetic polymers exhibit a certain degree of biodegradability, and they are typically characterized by ester (-COO), amide (-CONH), and ether (-COC-) bonds. The overall challenge is to manufacture synthetic polymers that contain bonds reminiscent of those present in natural polymers, so that microbial enzymes recognize them, enhancing thereby the polymer's biodegradability.

A couple of examples of synthetic polymers that are (to some extent) biodegradable are polylactic acid (see Fig. 13.12), poly(lactic acid-co-glycolic acid) (see Fig. 13.13), polyvinyl alcohol (see Fig. 13.11), polycaprolactone, poly(propylene fumarate), poly(ester-co-carbonate) and polyphosphazenes.

13.4 Alcohols

Alcohols are characterized by their functional group -OH (the hydroxyl group), and their general molecular formula is written as $C_nH_{2n+1}OH$ (with $n \in \{1, \cdots, 6\}$). The first six alcohols with one -OH group attached to the first carbon (C) atom are methanol (CH_3OH), ethanol (C_2H_5OH), propan-1-ol (C_3H_7OH), butan-1-ol (C_4H_9OH), pentan-1-ol ($C_5H_{11}OH$), and hexan-1-ol ($C_6H_{13}OH$)—for more details on nomenclature, see section 13.1.3.

Ethanol is probably the most widely known alcohol for its use in alcoholic drinks, cosmetic and medical products (e.g., solvents, hand sanitizers, and disinfectants), and as a methylated spirit in stoves, glass cleaners, permanent ink removers, and camping lamps. Alcohols are furthermore useful as an additive fuel in diesel and gasoline combustion engines, given their significant flammability (see section 13.1.5).

Apart from their high flammability, another **physical property** is their solubility in water, which is the result of the fact that alcohols and water are miscible liquids, as they are both polar compounds (see section 8.1). Moreover, their solubility *decreases* with a *longer* carbon chain, since the inter-molecular forces (see section 6.6) grow *stronger* with an *increasing* chain length. The same trend is observed when it comes to their boiling points, i.e., adding *more* carbon (C) atoms to the alcohols implies a *rising* pattern in their boiling points—put differently, their trend in volatility declines (see Table 13.3).

In terms of their **chemical properties**, alcohols can react with carboxylic acids to produce esters (see section 13.5), oxidize into carboxylic acids, and dehydrate to form alkenes—conversely, alcohols can be made from the hydration of alkenes (as well as through the process of fermentation). What is more, section 13.1.4 shows what the generic equation for the complete combustion of alcohols looks like.

In this section, the **reaction of alcohols with sodium (Na) metal** is discussed in greater detail. Just as one hydrogen (H) atom is replaced by one sodium atom when sodium (Na) reacts with water (H_2O), the sodium (Na) atom takes the place of the hydrogen (H) atom within the hydroxyl group (-OH) when reacting with alcohols. Similar to the reaction with water, hydrogen gas (H_2) is produced during this process. As an example, the below equation illustrates the reaction between methanol (CH_3OH) and sodium (Na):

$$\begin{cases} \text{Reaction with } \textit{water}\text{:} & 2\,\mathrm{Na}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{NaOH}(aq) + \mathrm{H_2}(g) \\ \text{Reaction with } \textit{methanol}\text{:} & 2\,\mathrm{Na}(s) + 2\,\mathrm{CH_3OH}(l) \longrightarrow 2\,\mathrm{CH_3ONa}(aq) + \mathrm{H_2}(g) \end{cases} \tag{13.15}$$

When one hydrogen (H) atom is removed from an alcohol, the anion that forms is called the **alkoxide anion**. The name of the respective alcohol ion then becomes *(base segment followed by the suffix -oxide)*. For instance, the ion of ethanol and pentan-1-ol is called ethoxide and pentoxide, respectively. In the example of Equation 13.15, the compound CH_3ONa is referred to as sodium methoxide.

Let us look at two additional examples whereby sodium (Na) reacts with the compounds propan-1-ol (C_3H_7OH) and hexan-1-ol ($C_6H_{13}OH$), respectively:

$$\begin{cases} \underset{\text{Sodium}}{2\,\mathrm{Na}(s)} & + & \underset{\text{Propan-1-ol}}{2\,\mathrm{C_3H_7OH}(l)} & \longrightarrow & \underset{\text{Sodium propoxide}}{2\,\mathrm{C_3H_7ONa}(aq)} & + & \underset{\text{Hydrogen gas}}{\mathrm{H_2}(g)} \\ \\ \underset{\text{Sodium}}{2\,\mathrm{Na}(s)} & + & \underset{\text{Hexan-1-ol}}{2\,\mathrm{C_6H_{13}OH}(l)} & \longrightarrow & \underset{\text{Sodium hexoxide}}{2\,\mathrm{C_6H_{13}ONa}(aq)} & + & \underset{\text{Hydrogen gas}}{\mathrm{H_2}(g)} \end{cases} \tag{13.16}$$

Keep furthermore in mind that the reactivity with sodium (Na) metal *diminishes* as the carbon chain of the alcohol becomes *longer* due to stronger inter-molecular forces at play.

13.5 Carboxylic Acids

Carboxylic acids are another homologous series of organic compounds. These acids contain the functional group -COOH (the carboxyl group) at the end(ings) of their carbon chain, and their molecular formula is represented by the generic notation $C_nH_{2n+1}COOH$ (with $n \in \{0, \cdots, 5\}$).

The first six linear straight-chain carboxylic acids carrying only one carboxyl group are called methanoic acid ($HCOOH$), ethanoic acid (CH_3COOH), propanoic acid (C_2H_5COOH), butanoic acid (C_3H_7COOH), pentanoic acid (C_4H_9COOH), and hexanoic acid ($C_5H_{11}COOH$)—a more detailed explanation on nomenclature is provided in section 13.1.3.

In terms of their **practical applications**, let us consider the first three acids. Methanoic acid, which is naturally found in most ants and some species of bees, is mainly used as a preservative and anti-bacterial agent in livestock feed. Ethanoic acid is a component of vinegar and is equally introduced in anti-septics, solvents, paints, and coatings. Finally, propanoic acid serves as a preservative for both baked goods for human consumption and animal feed as well as an intermediate in the production of polymers called thermoplastics.

Regarding their **chemical characteristics**, carboxylic acids behave as *weak acids*, i.e., they only partially dissolve in water (see section 9.1). In the same spirit as Equation 9.1, we can therefore write the chemical reaction of the (partial) dissolution of, for instance, butanoic acid as follows:

$$\mathrm{C_3H_7COOH}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{C_3H_7COO^-}(aq) \tag{13.17}$$

As the carboxylic acid donates a proton (H^+) when placed in an aqueous solution, it leaves behind an anion. The name of the anion of the respective carboxylic acid has the general form of *(remove the suffix '-ic acid' from the name of the carboxylic acid and replace it by the suffix '-ate')*. For example, in the above Equation 13.17 the anion $C_3H_7COO^-$ is known as butanoate. Three additional examples are given below:

$$\left\{\begin{array}{lcll}
\underset{\text{Ethanoic acid}}{CH_3COOH(aq)} & \rightleftharpoons & \underset{\text{Hydrogen ion}}{H^+(aq)} & + \underset{\text{Ethanoate ion}}{CH_3COO^-(aq)} \\
\underset{\text{Propanoic acid}}{C_2H_5COOH(aq)} & \rightleftharpoons & \underset{\text{Hydrogen ion}}{H^+(aq)} & + \underset{\text{Propanoate ion}}{C_2H_5COO^-(aq)} \\
\underset{\text{Hexanoic acid}}{C_5H_{11}COOH(aq)} & \rightleftharpoons & \underset{\text{Hydrogen ion}}{H^+(aq)} & + \underset{\text{Hexanoate ion}}{C_5H_{11}COO^-(aq)}
\end{array}\right. \tag{13.18}$$

As pointed out in section 9.3, acids can react with metal hydroxides, metal oxides, metals, or carbonates to produce **salts**. Bear in mind that the reactions with weak acids, such as carboxylic acids, take place at a much slower rate relative to strong acids. The below four chemical reactions illustrate the formation of salts for each type of reactant base mentioned above:

$$\left\{\begin{array}{lclcll}
\underset{\text{Methanoic acid}}{2\,HCOOH(aq)} + & \underset{\text{Strontium hydroxide}}{Sr(OH)_2(aq)} & \longrightarrow & \underset{\text{Strontium methanoate}}{(HCOO)_2Sr(aq)} & + \underset{\text{Water}}{2\,H_2O(l)} & \\
\underset{\text{Hexanoic acid}}{6\,C_5H_{11}COOH(aq)} + & \underset{\text{Aluminum oxide}}{Al_2O_3(s)} & \longrightarrow & \underset{\text{Aluminum hexanoate}}{2\,(C_5H_{11}COO)_3Al(aq)} & + \underset{\text{Water}}{3\,H_2O(l)} & \\
\underset{\text{Butanoic acid}}{2\,C_3H_7COOH(aq)} + & \underset{\text{Calcium}}{Ca(s)} & \longrightarrow & \underset{\text{Calcium butanoate}}{(C_3H_7COO)_2Ca(aq)} & + \underset{\text{Hydrogen gas}}{H_2(g)} & \\
\underset{\text{Pentanoic acid}}{2\,C_4H_9COOH(aq)} + & \underset{\text{Barium carbonate}}{BaCO_3(s)} & \longrightarrow & \underset{\text{Barium pentanoate}}{(C_4H_9COO)_2Ba(aq)} & + \underset{\text{Carbon dioxide}}{CO_2(g)} & + \underset{\text{Water}}{H_2O(l)}
\end{array}\right. \tag{13.19}$$

As previously discussed in section 13.3.2, an ester bond is created through a condensation reaction when a carboxyl (-COOH) and a hydroxyl (-OH) group are merged. The same mechanism is at work when a carboxylic acid and an alcohol react, i.e., they form esters, which is called **esterification**, and these (reversible) chemical reactions usually occur in the presence of an acidic catalyst, such as sulphuric acid (H_2SO_4).

During this reaction, the carboxylic acid sheds the hydroxide anion (OH^-) from its carboxyl group (-COOH), whereas the alcohol removes the hydrogen cation (H^+) from its hydroxyl group (-OH), generating water (H_2O) in the process. The name of the produced ester has the general form *(the base segment of the alcohol followed by the suffix '-yl')-(the name of the ion of the respective carboxylic acid).*

For instance, the below chemical equation and full structural formula in Fig. 13.18 demonstrate the reaction between ethanoic acid (CH_3COOH) and propan-1-ol (C_3H_7OH), which results in the ester propyl-ethanoate and water.

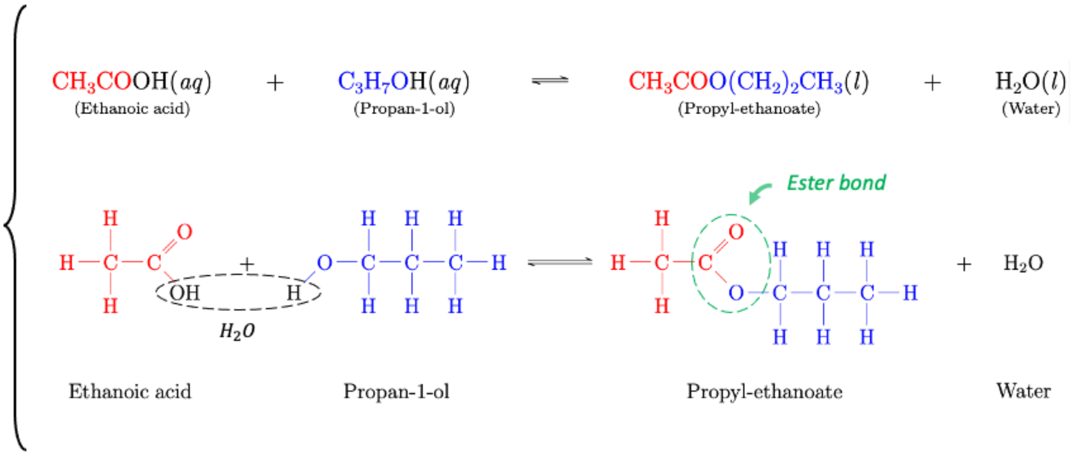


Figure 13.18: The formation of the ester propyl-ethanoate

Four additional examples of esterification are formulated below, whereby the esters butyl-methanoate ($C_5H_{10}O_2$), methyl-propanoate ($C_4H_8O_2$), pentyl-butanoate ($C_9H_{18}O_2$), and ethyl-pentanoate ($C_7H_{14}O_2$) are formed, respectively.

$$\left\{\begin{array}{ccccccc}
\underset{\text{Methanoic acid}}{HCOOH(aq)} & + & \underset{\text{Butan-1-ol}}{C_4H_9OH(aq)} & \rightleftharpoons & \underset{\text{Butyl-methanoate}}{HCOO(CH_2)_3CH_3(l)} & + & \underset{\text{Water}}{H_2O(l)} \\
\underset{\text{Propanoic acid}}{C_2H_5COOH(aq)} & + & \underset{\text{Methanol}}{CH_3OH(aq)} & \rightleftharpoons & \underset{\text{Methyl-propanoate}}{CH_3CH_2COOCH_3(l)} & + & \underset{\text{Water}}{H_2O(l)} \\
\underset{\text{Butanoic acid}}{C_3H_7COOH(aq)} & + & \underset{\text{Pentan-1-ol}}{C_5H_{11}OH(aq)} & \rightleftharpoons & \underset{\text{Pentyl-butanoate}}{CH_3(CH_2)_2COO(CH_2)_4CH_3(l)} & + & \underset{\text{Water}}{H_2O(l)} \\
\underset{\text{Pentanoic acid}}{C_4H_9COOH(aq)} & + & \underset{\text{Ethanol}}{C_2H_5OH(aq)} & \rightleftharpoons & \underset{\text{Ethyl-pentanoate}}{CH_3(CH_2)_3COOCH_2CH_3(l)} & + & \underset{\text{Water}}{H_2O(l)}
\end{array}\right. \tag{13.20}$$

Esters are characterized by their **fruity smell** and are naturally found in fruits. For instance, propyl-ethanoate (see Fig. 13.18) carries the scent of pears, methyl-butanoate that of apples, ethyl-butanoate that of pineapples, pentyl-butanoate (see Equation 13.20) that of apricots, and octyl-ethanoate that of oranges. This feature of esters explains why they are, for instance, often found in air fresheners and candles.

14 Metals

14.1 Trends in Reactivity

Metals encompass a broad variety of chemical elements, i.e., they can be subdivided into **alkali metals** (Group 1 of the Periodic Table), **alkaline earth metals** (Group 2), **transition metals** (Group 3 to 12), **other metals**, and **metalloids**, and form the majority of all known elements (see section 2.1). Metals are located mostly at the left-hand side and at the center of the Periodic Table, while non-metals aggregate at the right-hand side, with the non-metallic element hydrogen (H) being an exception, as it sits in Group 1 (see Fig. 2.1).

As discussed in section 2.3, the **ionization energy** of elements, which is the energy needed to cut loose a valence electron from the atom, generally *decreases down* a Group—as the atom grows larger in size, there is less electrostatic force between the nucleus and the valence electrons—and towards the *left* across a Period—a smaller nuclear charge reduces the electrostatic force between the nucleus and the valence electrons.

This structural pattern implies a *greater* tendency of the metals in Group 1 and 2 to lose their valence electron(s) and become positive ions (cations) with respect to the other metallic elements, since less energy is required to dislodge their valence electron(s). This means that the alkali and alkaline earth metals are among the **most reactive metals** within the Periodic Table.

In terms of the **ease of extraction of metals** from their metal compounds, which reside within minerals called *ores* in the Earth's crust, there is an *inverse relationship* with the metal's degree of reactivity. That is, much *more energy* is required to extract the *more reactive* metals, because they form *more stable* compounds within their respective ores. These metals are extracted by the method of *electrolysis* (see section 12), whereas the less reactive metals usually rely on chemical processes involving the element carbon (C) and heating.

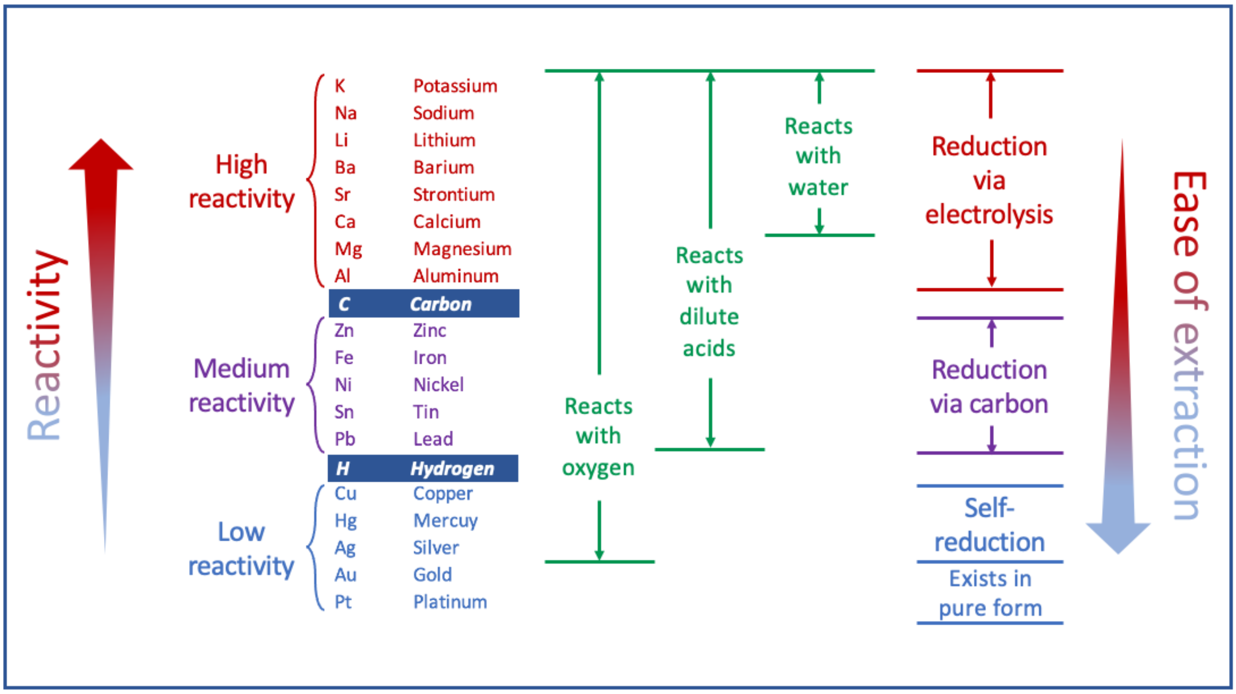


Figure 14.1: The trend in reactivity of metals

Typically, the metal compounds within the metal ores consist of the **oxides** of the respective metal. For instance, the metal iron (Fe) is extracted from the mineral iron(III) oxide (Fe_2O_3), a.k.a. hematite, the metal aluminum (Al) from the ore aluminum hydroxide ($Al(OH)_3$) called gibbsite, which is found within the rock formation known as bauxite, and the metal tin (Sn) from the mineral tin(IV) oxide (SnO_2), which is referred to as cassiterite.

As metal ions are cations, extraction processes always involve a **reduction** of the metal ion, which occurs through electrolysis, via carbon (C), or by self-reduction, whereby no external reducing agent is required (e.g., in the case of copper (Cu)).

For example, the extraction of iron (Fe) from hematite (Fe_2O_3) takes place at high temperatures in the presence of carbon monoxide (CO) and is represented by the following equations (with the oxidation state written in blue below the respective compounds):

$$\begin{cases} \text{Reduction:} & \underset{\text{(Fe: +III)}}{\mathrm{Fe_2O_3}(s)} + 6\,\mathrm{H^+}(aq) + 6\,\mathrm{e^-} \longrightarrow \underset{\text{(Fe: 0)}}{2\,\mathrm{Fe}(l)} + 3\,\mathrm{H_2O}(l) \\[2ex] \text{Oxidation:} & \underset{\text{(C: +II)}}{\mathrm{CO}(g)} + \mathrm{H_2O}(l) \longrightarrow \underset{\text{(C: +IV)}}{\mathrm{CO_2}(g)} + 2\,\mathrm{H^+}(aq) + 2\,\mathrm{e^-} \\[2ex] \text{Net equation:} & \mathrm{Fe_2O_3}(s) + 3\,\mathrm{CO}(g) \longrightarrow 2\,\mathrm{Fe}(l) + 3\,\mathrm{CO_2}(g) \end{cases} \tag{14.1}$$

A second example is the extraction of aluminum (Al) from the aluminum(III) oxide (Al_2O_3) ore called alumina (which is derived from the gibbsite ($Al(OH)_3$) mineral through heating). Since aluminum (Al) is more reactive than carbon (C), the extraction occurs via electrolysis (see Fig. 14.1). The respective equations can be written as follows:

$$\begin{cases} \text{Reduction (cathode):} & \underset{\text{(Al: +III)}}{\mathrm{Al^{3+}}(l)} + 3\,\mathrm{e^-} \longrightarrow \underset{\text{(Al: 0)}}{\mathrm{Al}(l)} \\[2ex] \text{Oxidation (anode):} & \underset{\text{(O: -II)}}{2\,\mathrm{O^{2-}}(l)} \longrightarrow \underset{\text{(O: 0)}}{\mathrm{O_2}(g)} + 4\,\mathrm{e^-} \\[2ex] \text{Net cell reaction:} & 2\,(\mathrm{Al_2O_3})(l) \longrightarrow 4\,\mathrm{Al}(l) + 3\,\mathrm{O_2}(g) \end{cases} \tag{14.2}$$

In fact, the reactivity series presented in Fig. 14.1 is a useful tool when it comes to **displacement reactions between metals**, whereby the *more reactive* metal displaces the *less reactive* metal from its compound.

For instance, given that magnesium (Mg) is higher up in the reactivity series than copper (Cu), it will displace copper (Cu) from the compound copper(II) oxide (CuO). As magnesium (Mg) is more reactive, it has a greater tendency to give up electrons and will therefore be oxidized. As a result, copper (Cu) is being reduced, as is shown in the following equations:

$$\left\{\begin{array}{ll}
\text{Full equation:} & \mathrm{Mg}(s) + \mathrm{CuO}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{MgO}(s) \\[2ex]
\text{Net ionic equation:} & \underset{\text{(Mg: 0)}}{\mathrm{Mg}(s)} + \underset{\text{(Cu: +II)}}{\mathrm{Cu}^{2+}(s)} \longrightarrow \underset{\text{(Cu: 0)}}{\mathrm{Cu}(s)} + \underset{\text{(Mg: +II)}}{\mathrm{Mg}^{2+}(s)} \\[2ex]
\text{Reduction:} & \underset{\text{(Cu: +II)}}{\mathrm{Cu}^{2+}(s)} + 2\,\mathrm{e}^- \longrightarrow \underset{\text{(Cu: 0)}}{\mathrm{Cu}(s)} \\[2ex]
\text{Oxidation:} & \underset{\text{(Mg: 0)}}{\mathrm{Mg}(s)} \longrightarrow \underset{\text{(Mg: +II)}}{\mathrm{Mg}^{2+}(s)} + 2\,\mathrm{e}^-
\end{array}\right. \tag{14.3}$$

Another example is known as the *thermite reaction*, whereby molten iron (Fe) is produced by reacting aluminum (Al) metal with hematite (Fe_2O_3). As aluminum (Al) is more reactive than iron (Fe), it makes a good reducing agent for iron (Fe):

$$\left\{\begin{array}{ll}
\text{Full equation:} & 2\,\mathrm{Al}(s) + \mathrm{Fe_2O_3}(s) \longrightarrow 2\,\mathrm{Fe}(l) + \mathrm{Al_2O_3}(s) \\[2ex]
\text{Net ionic equation:} & \underset{\text{(Al: 0)}}{\mathrm{Al}(s)} + \underset{\text{(Fe: +III)}}{\mathrm{Fe}^{3+}(s)} \longrightarrow \underset{\text{(Fe: 0)}}{\mathrm{Fe}(l)} + \underset{\text{(Al: +III)}}{\mathrm{Al}^{3+}(s)} \\[2ex]
\text{Reduction:} & \underset{\text{(Fe: +III)}}{\mathrm{Fe}^{3+}(s)} + 3\,\mathrm{e}^- \longrightarrow \underset{\text{(Fe: 0)}}{\mathrm{Fe}(l)} \\[2ex]
\text{Oxidation:} & \underset{\text{(Al: 0)}}{\mathrm{Al}(s)} \longrightarrow \underset{\text{(Al: +III)}}{\mathrm{Al}^{3+}(s)} + 3\,\mathrm{e}^-
\end{array}\right. \tag{14.4}$$

Displacement reactions can also occur **between metals and an aqueous solution of a metal's salt**. As a case in point, zinc (Zn) replaces tin (Sn) from its salt tin(II) chloride ($SnCl_2$), given that zinc (Zn) is the more reactive metal:

$$\left\{\begin{array}{ll}
\text{Full equation:} & \mathrm{Zn}(s) + \mathrm{SnCl_2}(aq) \longrightarrow \mathrm{Sn}(s) + \mathrm{ZnCl_2}(aq) \\[2ex]
\text{Net ionic equation:} & \underset{\text{(Zn: 0)}}{\mathrm{Zn}(s)} + \underset{\text{(Sn: +II)}}{\mathrm{Sn}^{2+}(aq)} \longrightarrow \underset{\text{(Sn: 0)}}{\mathrm{Sn}(s)} + \underset{\text{(Zn: +II)}}{\mathrm{Zn}^{2+}(aq)} \\[2ex]
\text{Reduction:} & \underset{\text{(Sn: +II)}}{\mathrm{Sn}^{2+}(aq)} + 2\,\mathrm{e}^- \longrightarrow \underset{\text{(Sn: 0)}}{\mathrm{Sn}(s)} \\[2ex]
\text{Oxidation:} & \underset{\text{(Zn: 0)}}{\mathrm{Zn}(s)} \longrightarrow \underset{\text{(Zn: +II)}}{\mathrm{Zn}^{2+}(aq)} + 2\,\mathrm{e}^-
\end{array}\right. \tag{14.5}$$

A second example is the displacement of silver (Ag) from its salt silver nitrate ($AgNO_3$) by the metal copper (Cu):

$$
\left\{
\begin{array}{ll}
\text{Full equation:} & \mathrm{Cu}(s) + 2\,\mathrm{AgNO_3}(aq) \longrightarrow 2\,\mathrm{Ag}(s) + \mathrm{Cu(NO_3)_2}(aq) \\
\text{Net ionic equation:} & \underset{\text{(Cu: 0)}}{\mathrm{Cu}(s)} + \underset{\text{(Ag: +I)}}{2\,\mathrm{Ag^+}(aq)} \longrightarrow \underset{\text{(Ag: 0)}}{2\,\mathrm{Ag}(s)} + \underset{\text{(Cu: +II)}}{\mathrm{Cu^{2+}}(aq)} \\
\text{Reduction:} & \underset{\text{(Ag: +I)}}{\mathrm{Ag^+}(aq)} + \mathrm{e^-} \longrightarrow \underset{\text{(Ag: 0)}}{\mathrm{Ag}(s)} \\
\text{Oxidation:} & \underset{\text{(Cu: 0)}}{\mathrm{Cu}(s)} \longrightarrow \underset{\text{(Cu: +II)}}{\mathrm{Cu^{2+}}(aq)} + 2\,\mathrm{e^-}
\end{array}
\right.
\tag{14.6}
$$

Conversely, it is also possible to **construct a reactivity series** based on experimental data generated by a number of displacement reactions. Suppose that the below Table 14.1 reflects the outcome of a number of experiments on five metals, i.e., A, B, C, D, and E, whereby the first column is listing the metals and the first row an oxide or salt of the respective metal.

Table 14.1: The outcome of a number of hypothetical displacement reactions

	Oxide/salt of metal A	**Oxide/salt of metal B**	**Oxide/salt of metal C**	**Oxide/salt of metal D**	**Oxide/salt of metal E**
Metal A	X	A replaces B	A replaces C	No reaction	A replaces E
Metal B	No reaction	X	B replaces C	No reaction	B replaces E
Metal C	No reaction	No reaction	X	No reaction	No reaction
Metal D	D replaces A	D replaces B	D replaces C	X	D replaces E
Metal E	No reaction	No reaction	E replaces C	No reaction	X

Knowing that only more reactive metals can displace the less reactive metals from their oxides or salts, the order of reactivity of the five metals can be determined. Looking at the row of metal C, it appears that it is unable to displace any of the four other metals, which implies that it is the least reactive metal of them all. Similarly, since metal D displaces all of the four other metals, it must be the most reactive one. Concerning metal A, B, and E, they are able to displace three, two, and one other metal(s), respectively, which implies that they take up position two, three, and four, respectively, in the reactivity series. As a result, the *order of reactivity* of these five metals is: $D > A > B > E > C$.

14.2 Properties and Uses

14.2.1 Physical Properties

In terms of their **physical properties**, metals are generally lustrous (shiny), hard (Group 1 metals form an exception: see section 7.1), strong, malleable (i.e., the ability of being deformed), ductile (i.e., the ability of being drawn into wires), sonorous, and good thermal and electrical conductors (see section 6.5).

Due to their **metallic luster**, metals, such as gold (Au) and silver (Ag), are used in decorations and jewelry. Moreover, as the valence electrons of metals easily reflect incoming photons of light, they make good coating materials for mirrors, as in the case of highly-polished silver (Ag), aluminum (Al), and chromium (Cr).

Metals are overall **hard and strong**, which implies that they are relatively difficult to cut, e.g., titanium (Ti) and tungsten (W) as opposed to the alkali and alkaline earth metals, and that they can serve as construction materials for heavy machinery, railway tracks, buildings, and bridges, such as the metals iron (Fe), aluminum (Al), lead (Pb), and copper (Cu). Note that gold (Au) and silver (Ag) are soft metals and thus unfit for construction applications.

Their pronounced **malleability** allows metals to be beaten into (very) thin metal sheets. In fact, gold (Au) and silver (Ag) are among the most malleable metals, making them particularly useful for jewelry. Another example is aluminum (Al), which is incorporated not only in the wrappings of medicines, food products, and chocolates but also in the metal body of vehicles, together with iron (Fe). A related physical property is **ductility** with gold (Au) and platinum (Pt) being the most ductile metals. The elements that are generally used to draw metal wires include copper (Cu), and often also iron (Fe), nickel (Ni), silver (Ag), or aluminum (Al).

When being hit, metals produce a ringing sound, i.e., they are **sonorous**, which makes them suitable for the construction of bells, metal gongs, cymbals, and pipe organs, which contain copper (Cu) and tin (Sn), as well as trombones, clarinets, tubas, and trumpets, which are made of copper (Cu), zinc (Zn), and sometimes nickel (Ni).

What is more, as copper (Cu), gold (Au), silver (Ag), and aluminum (Al) are one of the best **electrical conductors**, the fine electrical connections in computer chips are usually made of gold (Au) or silver (Ag), while the electrical wiring in our homes typically consists of aluminum (Al) or copper (Cu). These four metals equally possess high **thermal conductivity**, which explains, for instance, why copper (Cu), aluminum (Al), but also iron (Fe) constitute the main materials from which cooking equipment is made.

Different metals are often melted together (or metals with non-metals) into new compounds called **alloys**, so that the individual characteristics of the constitutive metals are combined to give the respective alloy a unique set of physical and chemical properties. For example, the mixture of copper (Cu) and zinc (Zn) is known as the alloy *brass*, which is used, for instance, to make brass instruments, such as trombones and horns, as well as candle holders, and can also be found in electrical sockets, marine engines, and electrical violins.

Another metallic alloy is *bronze*, whose two main components are copper (Cu) and tin (Sn), and is used in bells, hammers, sculpture art, and aircraft engines. Alloys can equally be formed between metals and non-metals, such as *steel*, which consists of a mixture of iron (Fe) and carbon (C). Steel alloys are used, for example, in the construction of bridges, ships, oil platforms, washing machines, and surgical scalpels.

14.2.2 Chemical Properties

When it comes to the **chemical properties** of metals, the reaction of metals with oxygen, water, dilute acids, and common bases (see Fig. 14.1), among other reactions, impacts the way in which these metals are used in our everyday life. Before providing some examples, let us first delve into some of these chemical reactions.

Almost all metals, bar gold (Au) and platinum (Pt), **react with oxygen (O_2)** to form metal oxides, i.e., the metals are oxidized as they give up their electrons. The below five examples provide the chemical equations for the oxidation of the metals sodium (Na), barium (Ba), aluminum (Al), iron (Fe), and silver (Ag):

$$\begin{cases} 4\,\mathrm{Na}(s) & + & \mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{Na_2O}(s) \\ 2\,\mathrm{Ba}(s) & + & \mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{BaO}(s) \\ 4\,\mathrm{Al}(s) & + & 3\,\mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{Al_2O_3}(s) \\ 4\,\mathrm{Fe}(s) & + & 3\,\mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{Fe_2O_3}(s) \\ 4\,\mathrm{Ag}(s) & + & \mathrm{O_2}(g) & \longrightarrow & 2\,\mathrm{Ag_2O}(s) \end{cases} \tag{14.7}$$

The **reaction of metals with water (H_2O)** depends on the temperature and the physical state of the water. The most reactive metals above magnesium (Mg) in the reactivity series (see Fig. 14.1) react readily with *cold water* to form metal hydroxides and hydrogen gas (H_2). From all the metals below calcium (Ca), only magnesium (Mg) and aluminum (Al) react with *heated water* to produce metal hydroxides. Finally, only the metals higher up than lead (Pb) react with *steam* to form metal oxides—bear in mind that the reactions between the metals above magnesium (Mg) and steam are extremely vigorous. A couple of examples are included below:

$$\begin{array}{ll} \textit{Cold water} & \begin{cases} 2\,\mathrm{K}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{KOH}(aq) + \mathrm{H_2}(g) \\ \mathrm{Ca}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Ca(OH)_2}(aq) + \mathrm{H_2}(g) \end{cases} \\ \\ \textit{Heated water} & \begin{cases} \mathrm{Mg}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{Mg(OH)_2}(s) + \mathrm{H_2}(g) \\ 2\,\mathrm{Al}(s) + 6\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Al(OH)_3}(s) + 3\,\mathrm{H_2}(g) \end{cases} \\ \\ \textit{Steam} & \begin{cases} \mathrm{Mg}(s) + \mathrm{H_2O}(g) \longrightarrow \mathrm{MgO}(s) + \mathrm{H_2}(g) \\ 2\,\mathrm{Al}(s) + 3\,\mathrm{H_2O}(g) \longrightarrow \mathrm{Al_2O_3}(s) + 3\,\mathrm{H_2}(g) \\ \mathrm{Zn}(s) + \mathrm{H_2O}(g) \longrightarrow \mathrm{ZnO}(s) + \mathrm{H_2}(g) \\ 3\,\mathrm{Fe}(s) + 4\,\mathrm{H_2O}(g) \longrightarrow \mathrm{Fe_3O_4}(s) + 4\,\mathrm{H_2}(g) \end{cases} \end{array} \tag{14.8}$$

In terms of **reactions with dilute acids**, such as dilute hydrochloric acid (HCl), sulphuric acid (H_2SO_4), and nitric acid (HNO_3), all the metals below magnesium (Mg) and above copper (Cu) only slowly react with cold dilute acids. However, their reactivity is enhanced when the acid is heated. In contrast, the metals above aluminum (Al) react very strongly with cold dilute acids, while those below lead (Pb) do not react with dilute acids at all. An exception is the reaction of copper (Cu) with concentrated nitric acid. When metals react with dilute acids, they form salts and hydrogen gas (H_2)—with the exception of copper (Cu)—as previously examined in reaction 9.18 (see section 9.3):

$$\begin{cases} \mathrm{Sr}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{SrSO_4}(aq) + \mathrm{H_2}(g) \\ \mathrm{Ni}(s) + 2\,\mathrm{HCl}(aq) \longrightarrow \mathrm{NiCl_2}(aq) + \mathrm{H_2}(g) \\ \mathrm{Pb}(s) + 2\,\mathrm{HCl}(aq) \longrightarrow \mathrm{PbCl_2}(aq) + \mathrm{H_2}(g) \\ \mathrm{Cu}(s) + 4\,\mathrm{HNO_3}(aq) \longrightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{NO_2}(g) + 2\,\mathrm{H_2O}(l) \end{cases} \tag{14.9}$$

One important practical implication of the specific chemical properties of metals is the approach adopted towards the prevention of **corrosion**, which is the oxidation of metals in the presence of both atmospheric oxygen (O_2) and water (H_2O). Put differently, corrosion means that the metals lose mass in the form of electrons.

In the case of iron (Fe) and steel alloys, the produced oxide is referred to as *rust*, and with regard to silver (Ag) and copper (Cu), it is called tarnish and verdigris, respectively. Chemically, rust is hydrated iron(III) oxide ($Fe_2O_3 \cdot H_2O$) and is formed as follows:

- Step 1: Iron (Fe) is oxidized in the presence of moist

  $\mathrm{Fe}(s) \longrightarrow \mathrm{Fe^{2+}}(aq) + 2\,\mathrm{e^-}$

- Step 2: Oxygen (O_2) is reduced

  $\mathrm{O_2}(g) + 2\,\mathrm{H_2O}(l) + 4\,\mathrm{e^-} \longrightarrow 4\,\mathrm{OH^-}(aq)$

- Step 3: Combing Step 1 and 2 produces iron(II) hydroxide ($Fe(OH)_2$) (14.10)

  $2\,\mathrm{Fe}(s) + \mathrm{O_2}(g) + 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Fe(OH)_2}(s)$

- Step 4: Iron(II) hydroxide ($Fe(OH)_2$) is further oxidized and turns into rust

  $4\,\mathrm{Fe(OH)_2}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Fe_2O_3 \cdot H_2O}(s) + 2\,\mathrm{H_2O}(l)$

- Step 5: The full equation for the formation of rust

  $4\,\mathrm{Fe}(s) + 3\,\mathrm{O_2}(g) + 2\,\mathrm{H_2O}(l) \longrightarrow 2\,\mathrm{Fe_2O_3 \cdot H_2O}(s)$

Even though aluminum (Al), chromium (Cr), and zinc (Zn) corrode more easily than iron (Fe)—this is reflected by their position in the reactivity series in Fig. 14.1—the outer layer of the metal oxide is sufficiently *stable* to protect the inner metal from further corrosion. In the case of iron (Fe), the rust is brittle and peels off, so that the inner metal becomes exposed and subsequently oxidized.

There are broadly speaking three ways to circumvent rusting and corrosion: installing a physical barrier between the metal and its surroundings, cathodic protection, and altering the type of metal used.

Applying a protective layer onto the metal can be done by painting, oiling and greasing, and electroplating (see section 12.4). Examples include the painting of an iron garden fence, greasing machine parts or oiling screws and bolts, and tin (Sn) or chromium (Cr) plating of a bicycle bell, a water tap, or a car grill.

Cathodic protection implies that the metal to be protected, e.g., iron (Fe), takes on the role of a cathode, so that any metal cations (Fe^{2+}) formed are reduced to metal atoms. This can be achieved through galvanization or sacrificial protection.

Galvanization refers to the situation whereby the metal that is in need of protection, e.g., iron (Fe), is coated with another more reactive metal, e.g., zinc (Zn). As a result, zinc (Zn) gets oxidized instead of iron (Fe), and the available electrons can reduce any iron cations (Fe^{2+}).

Sacrificial protection is based on the same principle, whereby the anode, which is typically magnesium (Mg) or zinc (Zn), is physically connected to the cathode through a wire or directly attached to the cathode. For instance, zinc (Zn) blocks are often attached to the hull of a ship, and magnesium (Mg) pipes are connected to underground pipelines.

The third prevention method infers the modification of the type of material by adding other metals, i.e., **alloying**. As pointed out previously, alloys possess unique properties that differ from those of their individual components. For example, kitchen utensils made of iron (Fe) would most certainly rust, whereas the alloy stainless steel, which is a mixture of iron (Fe), nickel (Ni), and chromium (Cr), makes a more suitable material since it prevents rusting.

14.3 Transition Metals

The chemical elements within the Periodic Table whose highest energy subshell consists of the d subshell, i.e., Groups 3 to 12, are collectively called the d-block (see section 2.2). Within the d-block, most of the elements are known as **transition metals**, which are defined as elements that have *at least one stable ion with a partially filled d-subshell.* For instance, iron (Fe) and niobium (Nb) are transition metals, while zinc (Zn) and yttrium (Y) are d-block elements but not transition metals, because the d subshell of the only stable ion they have is *either completely filled or empty*:

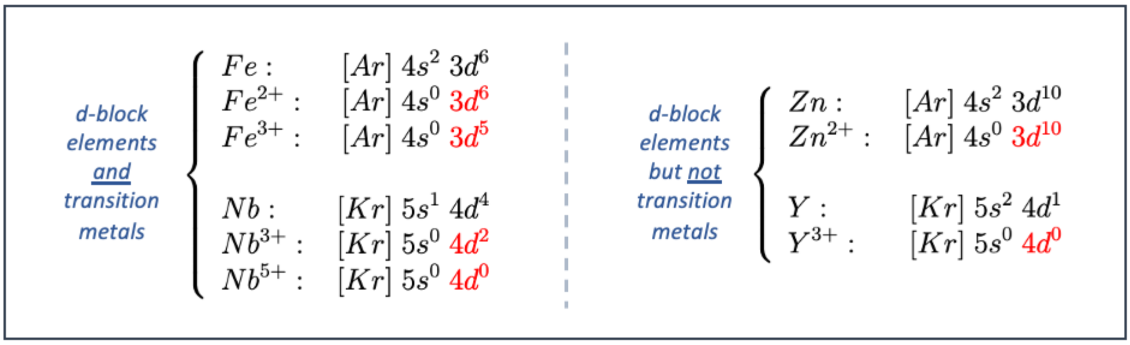


Figure 14.2: The difference between transition and d-block elements

The above definition means that transition metals can effectively transition into different oxidation states, whereby the **respective ions are stable**. Not only that, the transition metals often give rise to **coloured compounds** depending on their oxidation state. In Table 14.2, five transition metals are listed, mentioning some of their oxidation states together with the respective stable ion as well as the accompanying colour of that particular oxidation state.

Table 14.2: Five transition metals with some of their oxidation states

Transition Metal	**Oxidation State**	**Ion**	**Colour**
Manganese (Mn)	+II	$Mn^{2+}(aq)$	Pale pink
	+IV	$Mn^{4+}(aq)$	Brown
	+VII	$[MnO_4]^{-}(aq)$	Purple
Cobalt (Co)	+II	$Co^{2+}(aq)$	Pink
	+III	$Co^{3+}(aq)$	Green
Chromium (Cr)	+II	$Cr^{2+}(aq)$	Blue
	+III	$Cr^{3+}(aq)$	Green
	+VI	$[CrO_4]^{2-}(aq)$	Orange
Vanadium (V)	+II	$V^{2+}(aq)$	Violet
	+III	$V^{3+}(aq)$	Green
	+IV	$VO^{2+}(aq)$	Blue
	+V	$VO_2^{+}(aq)$	Yellow
Copper (Cu)	+I	$Cu^{+}(aq)$	Green
	+II	$Cu^{2+}(aq)$	Blue

A third characteristic of transition metals is the fact that they are commonly used as **catalysts in chemical reactions** (see section 10.4). A distinction is made between catalysts that find themselves either in a different physical state as that of the reactants, i.e., *heterogeneous catalysts*, or in the same phase, i.e., *homogeneous catalysts*. Three examples of heterogeneous catalysts are solid iron (Fe) during the production process of ammonia (NH_3), which is known as the Haber process, solid nickel (Ni) for the hydrogenation (see section 13.2) of ethene (C_2H_4), and solid manganese(IV) oxide (MnO_2) in the decomposition of hydrogen peroxide (H_2O_2):

$$\left\{\begin{array}{ccccc}
\underset{\text{nitrogen}}{N_2(g)} & + & \underset{\text{hydrogen}}{3\,H_2(g)} & \xrightleftharpoons{Fe(s)} & \underset{\text{ammonia}}{2\,NH_3(g)} \\[1em]
\underset{\text{ethene}}{C_2H_4(g)} & + & \underset{\text{hydrogen}}{H_2(g)} & \xrightarrow{Ni(s)} & \underset{\text{ethane}}{C_2H_6(g)} \\[1em]
\underset{\text{hydrogen peroxide}}{2\,H_2O_2(aq)} & \xrightarrow{MnO2(s)} & \underset{\text{water}}{2\,H_2O(l)} & + & \underset{\text{oxygen}}{O_2(g)}
\end{array}\right. \tag{14.11}$$

Two examples of homogeneous catalysts include aqueous iron(II) ions ($Fe^{2+}(aq)$) for the formation of sulphate ions (SO_4^{2-}) and iodine (I_2), and aqueous cobalt(II) ions ($Co^{2+}(aq)$) for the production of methanoate ions ($HCOO^-$). The chemical equations of the first example are as follows:

$$\left\{\begin{array}{ll}
\text{Oxidation of Fe}^{2+}: & \underset{\text{peroxydisulphate ion}}{S_2O_8^{2-}(aq)} + \underset{\text{iron(II) ion}}{2\,Fe^{2+}(aq)} \longrightarrow \underset{\text{sulphate ion}}{2\,SO_4^{2-}(aq)} + \underset{\text{iron(III) ion}}{2\,Fe^{3+}(aq)} \\
\text{Reduction of Fe}^{3+}: & \underset{\text{iodide ion}}{2\,I^-(aq)} + \underset{\text{iron(III) ion}}{2\,Fe^{3+}(aq)} \longrightarrow \underset{\text{iodine}}{I_2(aq)} + \underset{\text{iron(II) ion}}{2\,Fe^{2+}(aq)} \\
\text{Net equation:} & \underset{\text{peroxydisulphate ion}}{S_2O_8^{2-}(aq)} + \underset{\text{iodide ion}}{2\,I^-(aq)} \longrightarrow \underset{\text{sulphate ion}}{2\,SO_4^{2-}(aq)} + \underset{\text{iodine}}{I_2(aq)}
\end{array}\right. \tag{14.12}$$

The chemical equations of the second example of homogeneous catalysis are provided in the following three steps:

- Step 1: The cobalt(II) ion is oxidized

  $$\underset{\text{hydrogen peroxide}}{H_2O_2(aq)} + \underset{\text{hydrogen}}{2\,H^+(aq)} + \underset{\text{cobalt(II) ion}}{2\,Co^{2+}(aq)} \longrightarrow \underset{\text{water}}{2\,H_2O(l)} + \underset{\text{cobalt(III) ion}}{2\,Co^{3+}(aq)}$$

- Step 2: The cobalt(III) ion is reduced

  $$\underset{\text{tartrate ion}}{C_4H_4O_6^{2-}(aq)} + \underset{\text{water}}{2\,H_2O(l)} + \underset{\text{cobalt(III) ion}}{6\,Co^{3+}(aq)} \longrightarrow \underset{\text{carbon dioxide}}{2\,CO_2(g)} + \underset{\text{methanoate ion}}{2\,HCOO^-(aq)} + \underset{\text{hydrogen}}{6\,H^+(aq)} + \underset{\text{cobalt(II) ion}}{6\,Co^{2+}(aq)}$$

- Step 3: Combing Step 1 and 2 gives the net equation

  $$\underset{\text{tartrate ion}}{C_4H_4O_6^{2-}(aq)} + \underset{\text{hydrogen peroxide}}{3\,H_2O_2(aq)} \longrightarrow \underset{\text{carbon dioxide}}{2\,CO_2(g)} + \underset{\text{methanoate ion}}{2\,HCOO^-(aq)} + \underset{\text{water}}{4\,H_2O(l)}$$

15 Particle Theory

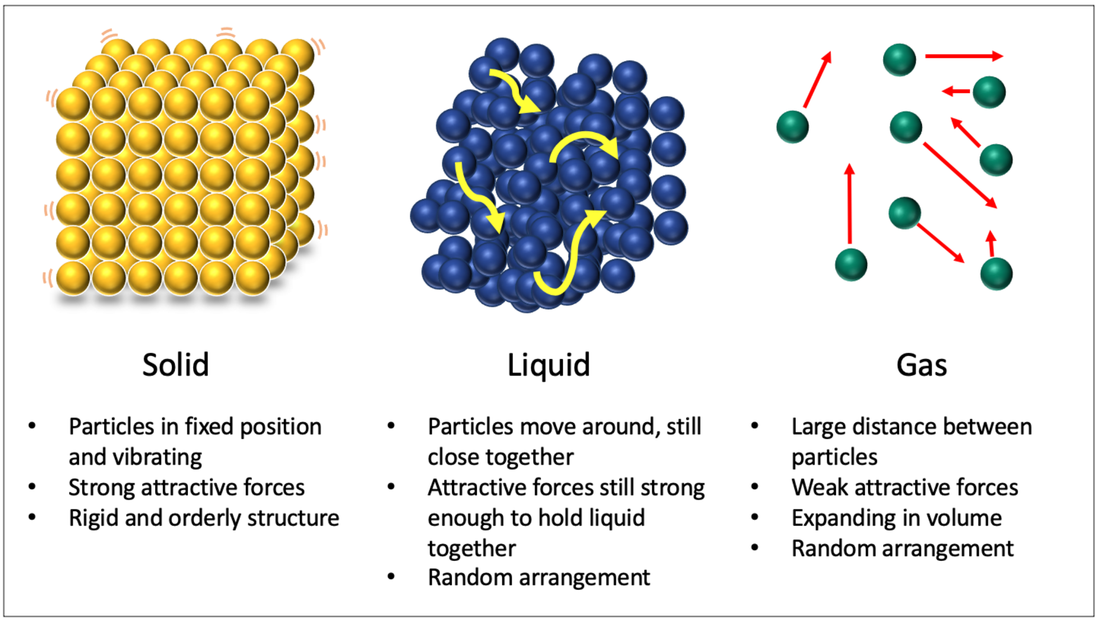
15.1 States of Matter

In general, the matter that we observe around us comes in three states: solid, liquid, and gas. At the microscopic level, matter is made of particles, which can exist either in a fundamental form, such as electrons, or in a more aggregate form, e.g., atoms, molecules, and ions. The specific *arrangement and behaviour* of particles in matter determine whether matter is classified as a solid, liquid, or gas.

In **solids**, particles are closely packed together and remain in a locked position—an exception are individual electrons in metals, which can easily move around (see section 6.5). Typically, this gives rise to a material with a microscopically regular pattern; very orderly solids are said to be crystalline. Although they stay put in their location, there is still room though for the particles to vibrate, which they do as a result of their thermal energy. Because of the overall rigid structure, not only can a solid maintain its own shape and volume when it is placed in a container, but it is also strong, hard to press together, and difficult to break apart.

In **liquids**, the particles are less tightly pressed together than in solids and move around rather easily, which leads to a random microscopic arrangement. In other words, physically breaking up a liquid is done effortlessly (as you can tell from holding your hand under a tap of running water). Another difference with solids is that when a liquid of a certain volume is introduced in a container, it takes on the shape of the container. Yet, it retains its volume—much like solids, liquids have a fixed volume.

The molecules in matter are held together by weak inter-molecular bonds (see section 6.6). As a matter of fact, the attractive inter-molecular forces in liquids lose a bit of their strength with respect to solids, since the particles are no longer located in fixed positions. However, they are still strong enough to keep the ensemble of particles from disintegrating. Nonetheless, both liquids and solids are difficult to compress, given that the spacing between particles is minimal.



- Particles in fixed position and vibrating
- Strong attractive forces
- Rigid and orderly structure

- Particles move around, still close together
- Attractive forces still strong enough to hold liquid together
- Random arrangement

- Large distance between particles
- Weak attractive forces
- Expanding in volume
- Random arrangement

Figure 15.1: The different states of matter

In **gases**, the distance between particles significantly increases, which enables them to move around with much higher velocities. This also means that a gas can be easily compressed and that its microscopic arrangement is completely random. The attractive inter-molecular forces in gases are now no longer sufficiently strong to hold the gas together, so that a gas naturally expands. As a result, and contrary to solids and liquids, when a gas is inserted in a container, it does not maintain its volume and is dispersed across the entire container until its volume matches that of the container.

In hindsight, the final state of matter essentially depends on the specific interplay between the kinetic energy of the particles, which drives them apart, and the inter-molecular forces involved, which draw the particles closer together. In gases, the kinetic energy gains the upper hand, while solids are firmly disciplined by the inter-molecular forces, with liquids somewhere stuck in the middle.

15.2 Changes of State

A **state change or phase change** refers to the moment of transition between two states of matter. Table 15.1 sums up the six different state changes that can occur for the three states of matter that we discussed in section 15.1, i.e., solids, liquids, and gases.

Table 15.1: The six different state changes

State Change	Name	Example
Solid to liquid	Melting	Ice to water
Solid to gas	Sublimation	Dry ice at room temperature
Liquid to solid	Freezing	Water to ice
Liquid to gas	Vaporization	Water to steam
Gas to solid	Deposition	Water vapour to ice
Gas to liquid	Condensation	Water vapour to dew

The **melting point** of a material substance is defined as the temperature at which the substance transitions from its solid into its liquid state at atmospheric pressure (i.e., the pressure of the Earth's atmosphere at sea level). What happens at microscopical level is that the particles in the solid state gain additional kinetic energy as the temperature rises. When the average kinetic energy grows to the point where it is *able to overcome the attractive strength of the inter-molecular forces*, the particles start leaving their locked positions, which signals the *onset* of the melting stage—bear in mind that the average kinetic energy *during* the transition from a solid to a liquid state does not change, as we shall see below.

Table 15.2 below provides the melting points for a handful of different materials. Generally, the melting point *rises with the strength of the bonds.* That is, networks of covalent bonds result in very high melting points (e.g., carbon), while simple covalent compounds (e.g., ammonia) give the lowest melting points, as they are held together by weak inter-molecular forces. Bear in mind that melting is about overcoming the inter-molecular forces and does *not* imply breaking the chemical bonds *within* molecules—a notable exception are the giant structures of covalent bonds, whereby melting involves breaking the covalent bonds (see section 6.4.3). Therefore, the *stronger* the inter-molecular forces between the molecules, the *higher* the melting point.

Table 15.2: The melting points for different materials at atmospheric pressure

Substance	Melting Point (in °C)	Substance	Melting Point (in °C)
Aluminum	658	Lead	327
Ammonia	-77.7	Lithium	180.5
Bronze	910	Mercury	-38.8
Carbon	3,550	Nickel	1,455
Chloroform	-63.4	Nitrogen	-210
Copper	1,083	Palmitic acid	62.9
Glucose	146	Phosphorus	44.1
Gold	1,065	Polystyrene	240
Ice	0	Sand	1,550
Iron	1,538	Titanium	1,668

During **freezing**, the opposite process is taking place with respect to melting. As the temperature of the liquid drops, the average kinetic energy of the molecules decreases, so that the inter-molecular forces gradually gain in strength and the structure of the liquid becomes more and more rigid, i.e., more inter-molecular bonds are being formed. At the freezing point, the liquid substance effectively starts to transition from a liquid into a solid state—again, *during* freezing the average kinetic energy remains constant.

Although the melting point usually equals the freezing point, these two temperatures do not necessarily have to match. As a case in point, it is found that very pure water can reach temperatures well below 0°C and still remain liquid, even though water usually freezes at 0°C.

The **boiling point** of a substance refers to the temperature of a substance, measured at atmospheric pressure, whereby the average kinetic energy has reached the stage at which the particles become unimpeded by the inter-molecular forces and detach from the liquid to roam freely throughout the space around them. The corresponding state change is known as *vaporization*, which marks the transformation from a liquid into a gaseous state; as in the case of melting or freezing, *during* this transition, the average kinetic energy does not further increase.

Table 15.3: The boiling points for different materials at atmospheric pressure

Substance	Boiling Point (in °C)	Substance	Boiling Point (in °C)
Aluminum	2,327	Lead	1,740
Ammonia	-33.3	Lithium	1,336
Bronze	2,300	Mercury	357
Carbon	4,827	Nickel	2,730
Chloroform	61.1	Nitrogen	-196
Copper	2,595	Palmitic acid	351
Glucose	527.1	Phosphorus	279.7
Gold	2,700	Polystyrene	430
Water	100	Sand	2,230
Iron	2,861	Titanium	3,287

Table 15.3 supplies the boiling points of the substances mentioned in Table 15.2. Again, the *stronger* the inter-molecular forces, the *more elevated* the boiling point for a certain substance (bear in mind that other factors also have an influence, such as the shape of the molecule and its molecular weight). Since external pressure can influence the strength of the inter-molecular forces, a liquid on top of the Kilimanjaro mountain, where the atmospheric

pressure is *lower* compared to the sea level—it measures around 0.39 atm—boils at a *lower* temperature. If you would like to cook your food while enjoying the scenic view at an altitude of 5,896 m, you will in fact have to wait longer for your meal to be ready, given that the water boils at a lower temperature. Similarly, a pressure cooker operates at roughly 1.9 atm, which ensures that water boils at a higher temperature, reducing the time needed for food to cook, if that water were to be used for cooking.

Condensation is the reversed process of boiling, whereby the declining temperature of the gas is leading to growing inter-molecular forces, allowing the particles to be drawn closer to one another and form inter-molecular bonds. At the condensation point, the gas starts to transform into a liquid, and at the end of the process of condensation, the gas will have completely converted into a liquid. Note that also in the case of condensation, the average kinetic energy *during* the phase change remains unaltered.

The concept of **specific heat capacity** is used to identify the amount of energy required for a substance in a particular state of matter (per unit mass) to achieve a one degree Celsius increase in temperature—or, alternatively, the amount of energy released during a decrease of 1°C. However, at the moment of a phase change, even though the temperature stays *at a constant value*, additional energy is required (or released) to complete the transition between the different states. This energy is called **latent heat**, which is *not* kinetic energy (otherwise the temperature would rise) but a potential energy, i.e., a form of stored energy within the system, needed to *overcome the inter-molecular forces of the bonds between the neighbouring particles.*

The latent heat related to melting and freezing is called the **latent heat of fusion**, whereas the **latent heat of vaporization** indicates the required or released phase energy during either vaporization or condensation. The *higher* the strength of the inter-molecular forces, the *higher* the amount of energy required for the particles to break away either from their fixed locations within a solid or from the relatively loose positions within a liquid.

For any material, the latent heat of vaporization is always *larger* than the latent heat of fusion, since it requires much more energy to break *entirely* free from inter-molecular forces (which is the case for the phase of vaporization) rather than *weakening* the inter-molecular bond strength (which is the case for the phase of melting). Table 15.4 provides the latent heat of both fusion and vaporization for the substances mentioned in Table 15.3.

Table 15.4: The latent heat of fusion and vaporization for different materials (at 1 atm)

Substance	**Heat of Fusion (in kJ·kg^{-1})**	**Heat of Vaporization (in kJ·kg^{-1})**	**Substance**	**Heat of Fusion (in kJ·kg^{-1})**	**Heat of Vaporization (in kJ·kg^{-1})**
Aluminum	399.9	10,874	Lead	23.2	857.6
Ammonia	332.3	1,372	Lithium	432.2	21,023
Bronze	/	/	Mercury	11.4	295.3
Carbon	9,741	29,624	Nickel	297.6	6,310.8
Chloroform	73.7	263	Nitrogen	25.7	199.4
Copper	205.4	4,725.7	Palmitic acid	167.2	291.1
Glucose	110.6	652.3	Phosphorus	21.2	391.6
Gold	63.7	1,697.75	Polystyrene	132.1	348
Water	333	2,258	Sand	/	/
Iron	247.3	6,260.2	Titanium	322.8	8,795

16 Chemical Tests

16.1 Tests for Gases

In this section, various experimental tests are explored that help to establish the presence or absence of hydrogen (H_2), oxygen (O_2), carbon dioxide (CO_2), and chlorine gas (Cl_2).

To examine the presence of **hydrogen (H_2)**, which has no smell or colour, a wooden splint is lighted and held at the open end of a test tube that contains a certain mixture. Suppose that the reactants magnesium (Mg) and hydrochloric acid (HCl) are introduced in the test tube. According to the following equation, the test tube should possess traces of hydrogen gas:

$$\mathrm{Mg}(s) + 2\,\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2}(g) \tag{16.1}$$

The way to confirm the presence of hydrogen is by observing that the hydrogen gas *extinguishes the lighted splint*—this feature is not exclusive to hydrogen testing though—and that the burning of hydrogen is accompanied by a **squeaky, popping sound**—this is unique to hydrogen. The chemical reaction of the burning of hydrogen gas is given by the following equation:

$$2\,\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{H_2O}(l) \tag{16.2}$$

To experimentally find out whether a test tube holds **oxygen gas (O_2)**, which, similar to hydrogen, does not have any smell or colour, consider the following reaction whereby potassium chlorate ($KClO_3$) is heated:

$$2\,\mathrm{KClO_3}(s) \longrightarrow 2\,\mathrm{KCl}(s) + 3\,\mathrm{O_2}(g) \tag{16.3}$$

Apart from potassium chloride (KCl), also oxygen (O_2) should be produced. To test the presence of oxygen, an extinguished but still glowing splint is brought towards the open end of the test tube, and the confirmation of its presence would be reflected by a **rekindling of the glowing splint**. In fact, it is the *only gas* that is able to relight an extinguished splint.

To investigate the presence of **carbon dioxide gas (CO_2)**, which has no colour or smell just as hydrogen and oxygen, a number of tests are available. Suppose that methane gas (CH_4) is burnt, which produces carbon dioxide and water vapour:

$$\mathrm{CH_4}(g) + 2\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(g) \tag{16.4}$$

The two following tests are of a more general nature and do not uniquely establish the presence of carbon dioxide (CO_2). A first test consists of holding a lighted splint at the open end of the test tube, whereby any presence of carbon dioxide (CO_2) would *extinguish the flame*. Another way of probing its possible presence is exposing the gas to a moist blue litmus paper, which is kind of filter paper that aims to establish the alkalinity or acidity of a substance. If carbon dioxide (CO_2) is present, the *blue litmus paper turns red*, indicating an acid environment, because weak carbonic acid (H_2CO_3) is produced when the gas reacts with the moist of the paper:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \tag{16.5}$$

To definitively determine the presence of carbon dioxide (CO_2), there is a third, specific test whereby the mixture, which may or may not contain the gas, is introduced in limewater ($Ca(OH)_2$). If the carbon dioxide gas (CO_2) is present, the **colourless limewater converts into a white, cloudy solution**, forming during the process a solid precipitate of carbon carbonate ($CaCO_3$):

$$Ca(OH)_2(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l) \tag{16.6}$$

Finally, to study a mixture for the presence of the toxic **chlorine gas (Cl_2)**, which has a yellow-green colour and a pungent, irritating odour, there is a general and a specific test available. The gas can be produced, for instance, by letting bleaching powder ($CaOCl_2$) react with concentrated hydrochloric acid (HCl):

$$CaOCl_2(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + Cl_2(g) + H_2O(l) \tag{16.7}$$

First, the products can be submitted to a general, non-conclusive test of holding a lighted splint at the open end of the test tube. If the gas is indeed present, the *flame is extinguished*. The second, specific test for the presence of chlorine gas (Cl_2) is letting it interact with a moist blue litmus paper. Its presence is confirmed when **the blue litmus paper first turns red and then white, i.e., it is bleached**, as chlorine gas (Cl_2) is the *only gas* that bleaches the litmus paper.

The acidity established by the paper, i.e., it turns red, is a consequence of the reaction between the gas and the moist of the paper, which produces hydrochloric acid (HCl) as well as hypochlorous acid (HClO):

$$Cl_2(g) + H_2O(l) \rightleftharpoons HCl(aq) + HClO(aq) \tag{16.8}$$

16.2 Tests for Carbonate, Sulfate, and Halide Anions

In order to examine the presence of **carbonate anions ($\mathbf{CO_3^{2-}}$)** in a mixture or compound, **a diluted acid is added**, resulting in the creation of a salt, carbon dioxide (CO_2) and water (H_2O), as pointed out in Equation 9.16. If any gas is produced, it can be mixed with limewater, which turns into a white, cloudy solution in the case that the gas is carbon dioxide (CO_2), as discussed in section 16.1.

For example, if dilute sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) are mixed with copper(II) carbonate ($CuCO_3$) and zinc carbonate ($ZnCO_3$), respectively, carbon dioxide (CO_2) forms, so that the limewater test will come out positive:

$$\begin{cases} \mathrm{H_2SO_4}(aq) & + & \mathrm{CuCO_3}(s) & \longrightarrow & \mathrm{CuSO_4}(aq) & + & \mathrm{CO_2}(g) & + & \mathrm{H_2O}(l) \\ 2\,\mathrm{HCl}(aq) & + & \mathrm{ZnCO_3}(s) & \longrightarrow & \mathrm{ZnCl_2}(aq) & + & \mathrm{CO_2}(g) & + & \mathrm{H_2O}(l) \end{cases} \tag{16.9}$$

To probe a sample for the presence of **sulfate anions ($\mathbf{SO_4^{2-}}$)**, two steps are involved. First, diluted hydrochloric acid (HCl) is added so that any carbonate (CO_3^{2-}) or sulfite ions (SO_3^{2-}) are removed. Then, an aqueous solution of barium chloride ($BaCl_2$) is introduced into the sample. If any sulfate anions (SO_4^{2-}) are present, they will react with the barium cations (Ba^{2+}) and form a **white precipitate of barium sulfate ($\mathbf{BaSO_4}$)**.

For instance, adding barium chloride ($BaCl_2$) to a solution of potassium sulfate (K_2SO_4)—after it has been treated with diluted hydrochloric acid (HCl)—gives a positive test result, as a white precipitate of barium sulfate ($BaSO_4$) forms:

$$\mathrm{BaCl_2}(aq) + \mathrm{K_2SO_4}(aq) \longrightarrow 2\,\mathrm{KCl}(aq) + \mathrm{BaSO_4}(s) \tag{16.10}$$

To investigate the presence of the **halide anions chloride ($\mathbf{Cl^-}$), bromide ($\mathbf{Br^-}$), and iodide ($\mathbf{l^-}$)** in a mixture, again two steps are taken, similar to those in the test for sulfate anions.

In a first stage, the addition of dilute nitric acid (HNO_3) to the sample eliminates any carbonate (CO_3^{2-}) or sulfite ions (SO_3^{2-}). Next, silver nitrate ($AgNO_3$) is added, so that the silver cations (Ag^+) can react with the chloride (Cl^-), bromide (Br^-), or iodide (l^-) anions to form a **white, cream, or yellow precipitate of silver chloride (AgCl), silver bromide (AgBr), or silver iodide (Agl), respectively**.

For example, if silver nitrate ($AgNO_3$) is mixed with lithium chloride (LiCl), sodium bromide (NaBr), and potassium iodide (KI), respectively, a white, cream, and yellow precipitate of silver chloride (AgCl), silver bromide (AgBr), and silver iodide (Agl) forms, respectively:

$$
\left\{
\begin{array}{lllllll}
\mathrm{AgNO_3}(aq) & + & \mathrm{LiCl}(aq) & \longrightarrow & \underset{\text{white precipitate}}{\mathrm{AgCl}(s)} & + & \mathrm{LiNO_3}(aq) \\[2em]
\mathrm{AgNO_3}(aq) & + & \mathrm{NaBr}(aq) & \longrightarrow & \underset{\text{cream precipitate}}{\mathrm{AgBr}(s)} & + & \mathrm{NaNO_3}(aq) \\[2em]
\mathrm{AgNO_3}(aq) & + & \mathrm{KI}(aq) & \longrightarrow & \underset{\text{yellow precipitate}}{\mathrm{Agl}(s)} & + & \mathrm{KNO_3}(aq)
\end{array}
\right.
\tag{16.11}
$$

16.3 Tests for Metal Cations

To study the presence of metal cations in a certain solution, two tests are commonly used: adding an aqueous solution of sodium hydroxide (NaOH) to the sample, and the flame test.

In the first instance, **sodium hydroxide (NaOH)** is introduced into the solution. If a precipitate forms, some of the metal cations can be identified by its specific colour, while for some other metal cations, the precipitate turns white. In the absence of a precipitate, the metal cations may refer to the metal lithium (Li), sodium (Na), or potassium (K), which can be distinguished by the flame test (see below).

If the formed precipitate has a **blue, green, or brown colour**, the metal cations are **the copper(II) ion (Cu^{2+}), the iron(II) ion (Fe^{2+}), and the iron(III) ion (Fe^{3+}), respectively**. The following three examples show the reaction between sodium hydroxide (NaOH) and copper(II) chloride ($CuCl_2$), iron(II) bromide ($FeBr_2$), and iron(III) sulfate ($Fe_2(SO_4)_3$):

$$
\left\{
\begin{array}{lllllll}
\mathrm{CuCl_2}(aq) & + & 2\,\mathrm{NaOH}(aq) & \longrightarrow & \underset{\text{blue precipitate}}{\mathrm{Cu(OH)_2}(s)} & + & 2\,\mathrm{NaCl}(aq) \\[2em]
\mathrm{FeBr_2}(aq) & + & 2\,\mathrm{NaOH}(aq) & \longrightarrow & \underset{\text{green precipitate}}{\mathrm{Fe(OH)_2}(s)} & + & 2\,\mathrm{NaBr}(aq) \\[2em]
\mathrm{Fe_2(SO_4)_3}(aq) & + & 6\,\mathrm{NaOH}(aq) & \longrightarrow & \underset{\text{brown precipitate}}{2\,\mathrm{Fe(OH)_3}(s)} & + & 3\,\mathrm{Na_2SO_4}(aq)
\end{array}
\right.
\tag{16.12}
$$

For the metal cations of **magnesium (Mg^{2+}), aluminum (Al^{3+}), and calcium (Ca^{2+})**, the formed precipitate with sodium hydroxide **all turn white**. These three examples demonstrate how sodium hydroxide (NaOH) reacts with magnesium nitrate ($Mg(NO_3)_2$), aluminum iodide (AlI_3), and calcium chlorate ($Ca(ClO_3)_2$):

$$\begin{cases} \mathrm{Mg(NO_3)_2}(aq) + 2\,\mathrm{NaOH}(aq) \longrightarrow \underset{\text{white precipitate}}{\mathrm{Mg(OH)_2}(s)} + 2\,\mathrm{NaNO_3}(aq) \\ \mathrm{AlI_3}(aq) + 3\,\mathrm{NaOH}(aq) \longrightarrow \underset{\text{white precipitate}}{\mathrm{Al(OH)_3}(s)} + 3\,\mathrm{NaI}(aq) \\ \mathrm{Ca(ClO_3)_2}(aq) + 2\,\mathrm{NaOH}(aq) \longrightarrow \underset{\text{white precipitate}}{\mathrm{Ca(OH)_2}(s)} + 2\,\mathrm{NaClO_3}(aq) \end{cases} \tag{16.13}$$

In order to correctly assess which metal cation constitutes the white precipitate, the following tests can be implemented. To rule out aluminum cations (Al^{3+}), introducing additional solution of sodium hydroxide (NaOH) should not affect the sample, as an **excess of sodium hydroxide (NaOH) dissolves the aluminum precipitate**. To distinguish between magnesium (Mg^{2+}) and calcium cations (Ca^{2+}), the flame test, which is explained below, can indicate the particular type of metal: **magnesium cations (Mg^{2+}) exhibit no flame colour, while calcium cations (Ca^{2+}) produce a red-orange colour**.

The **flame test** consists of first dipping one end of a nichrome wire—nichrome is an alloy made of nickel (Ni), chromium (Cr), and sometimes iron (Fe)—in concentrated hydrochloric acid (HCl), then inserting it into the metal that is subject to examination, and finally holding the moist wire in a flame.

Given that the alkali metals produce no precipitate when mixed together with sodium hydroxide (NaOH), the flame test is used to differentiate amongst them. **Lithium (Li), sodium (Na), and potassium (K) produce a crimson red, yellow-orange, and lilac flame colour, respectively**.

Some of the other metals also produce flame colours, as already pointed out above in the case of calcium cations (Ca^{2+}). Other examples include **copper(II) cations** (Cu^{2+}), strontium cations (Sr^{2+}), and aluminum cations (Al^{3+}), which give a **bluish-green**, a brick red, and a silver-white flame colour, respectively.

16.4 Tests for Water

In order to examine the presence of water (H_2O), which in its liquid or gaseous form has no smell or colour, a general, non-conclusive test exists of the fact that water vapour extinguishes a lighted wooden splint.

However, to *uniquely* determine the presence of water, one way is to mix water or water vapour with anhydrous (pure) copper(II) sulfate ($CuSO_4$), which is a white powder and completely dry as it lacks any water. If the sample contains water, **the white powder of anhydrous copper(II) sulfate ($CuSO_4$) turns blue**. The chemical reaction is as follows:

$$\underset{\text{white powder}}{\mathrm{CuSO_4}(s) + 5\,\mathrm{H_2O}(l)} \rightleftharpoons \underset{\text{blue powder}}{\mathrm{CuSO_4 \cdot 5\,H_2O}(s)} \tag{16.14}$$

17 Air and Water

17.1 Composition of Dry Air

Dry air is air that lacks water (H_2O) and is found mainly in the upper layers of the atmosphere, i.e., the stratosphere (12km-48km above sea level), the mesosphere (48km-85km above sea level), and the lower parts of the thermosphere (85km-100km above sea level). About 90% of the water in the atmosphere is contained in its lowest layer, which is called the troposphere (0km-12km above sea level) and is also the region where most of the Earth's weather events take place, and roughly 99.9% of the mass of the entire atmosphere is contained within the two bottom layers combined, i.e., the troposphere and the stratosphere.

The **percentage composition of dry air** is equal to 78.08% of nitrogen (N_2), 20.95% of oxygen (O_2), 0.93% of argon (Ar), 0.035% of carbon dioxide (CO_2), and 0.005% of other substances, including neon (Ne), helium (He), krypton (Kr), nitrous oxide (N_2O), and methane (CH_4).

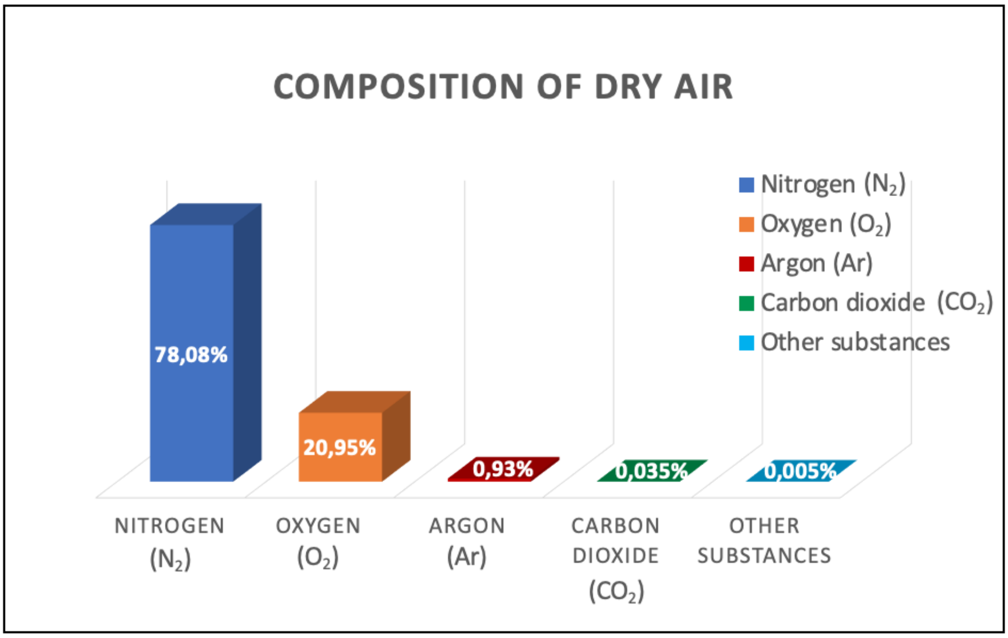


Figure 17.1: The percentage composition of dry air

The different components of dry air can be separated from one another through **fractional distillation** (see section 8.2), whereby the boiling or sublimation points of the various components act as the mechanism of separation (see Fig. 17.2). For this method to work, the dry air is gradually cooled until it reaches a temperature of -200°C, at which the air finds itself in a liquid state.

In a first stage, when the air gets to a temperature of -78.5°C, the carbon dioxide (CO_2) converts from its gaseous phase to a solid state, i.e., dry ice, and is removed from the sample—the phase change from gas to solid is referred to as deposition (see Table 15.1). The liquid air of -200°C is then transported to a fractional column, whereby the lower part is kept at a higher temperature (-185°C) compared to the upper part of the column (-190°C).

With the lowest boiling point of -196°C, nitrogen gas (N_2) is the first substance to be distilled off at the upper part of the fractional column. In a compartment below that of nitrogen, argon (Ar), which has a boiling point of -186°C, is the next gas to be distilled out. Finally, given that oxygen (O_2) boils at -183°C and that the lower part of the fractional column has a temperature of -185°C, oxygen is removed as a *liquid* at the bottom of the column.

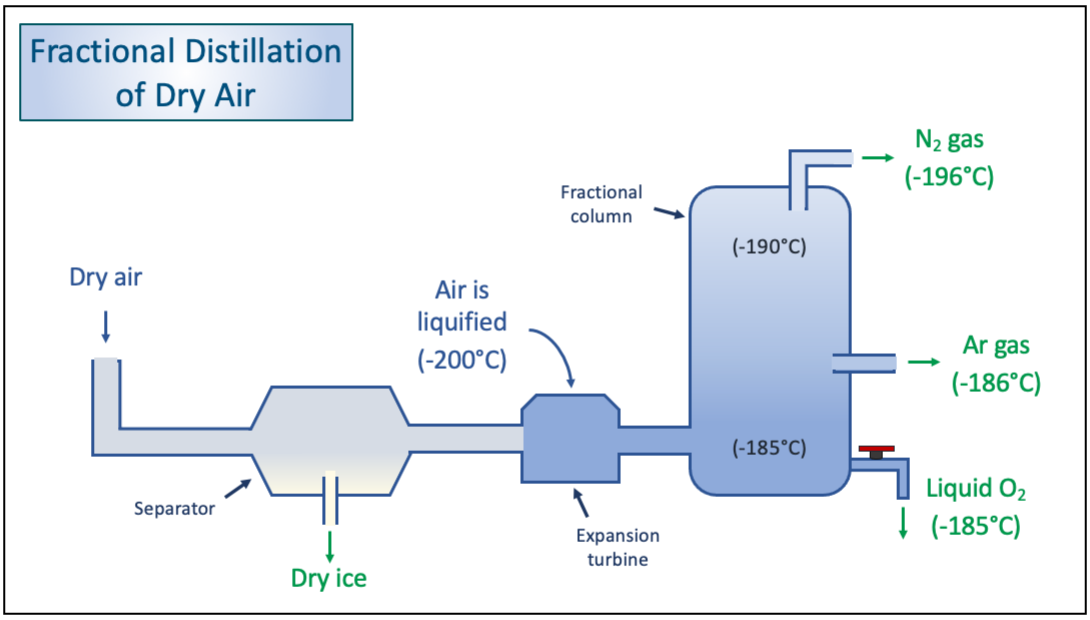


Figure 17.2: The fractional distillation of dry air

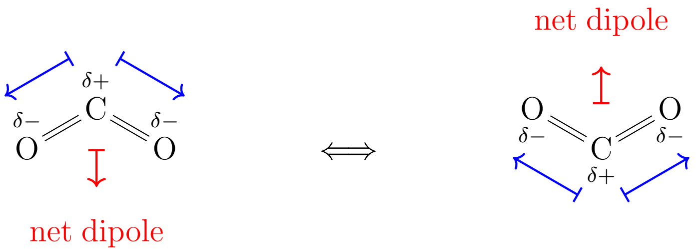
17.2 Greenhouse Gases

In section 6.6 on inter-molecular forces, it is explained that an electric dipole is created as the result of an asymmetry within the internal charge distribution of a compound. For instance, in the compound **carbon dioxide (CO_2)**, the oxygen (O) atom has a greater electronegative value (see section 5.3) than the carbon (C) atom, which means that the oxygen (O) atom in the O=C bond pulls harder on the bonding electrons than the carbon (C) atom. In other words, a **dipole** arises, which is schematically represented by an arrow that points from its positive side (δ^+) at the carbon (C) atom towards its negative side (δ^-) at the oxygen (O) atom.

$$\begin{array}{c} \longleftarrow\!\!\!\mid \;\; \mid\!\!\!\longrightarrow \\ \overset{\delta-}{\mathrm{O}}=\overset{\delta+}{\mathrm{C}}=\overset{\delta-}{\mathrm{O}} \end{array} \tag{17.1}$$

As carbon dioxide (CO_2) contains two O=C bonds and its geometric structure is linear, the two dipole moments point to opposite directions and cancel each other out, i.e., the net dipole moment of the compound is zero. Stated differently, the carbon dioxide (CO_2) compound has no permanent dipole moment in its resting position, i.e., it is a non-polar compound (see section 6.4.1).

However, as the bonds of compounds constantly stretch, bend, and twist—these movements of the bonds are called the **vibrational modes of the compound**—it is implied that the net dipole moment of the carbon dioxide (CO_2) compound can momentarily obtain a non-zero value. This means that the CO_2 compound is capable of creating an **oscillating electrical field**, which is depicted below in the case of the *bending* vibrational mode:



(17.2)

Oscillating electrical fields can interact with other oscillating electrical fields, as long as their frequencies, i.e., the rate of vibrating, line up. As a matter of fact, light, such as infrared light, visible light, or microwaves, is made of oscillating electromagnetic fields, which are entangled magnetic and electrical fields. This means that **light is able to interact with chemical compounds that produce oscillating electrical fields, such as carbon dioxide (CO_2), as long as the vibrational frequencies of the bonds align with the frequency of the light**.

A consequence of this alignment of frequencies is that the energy state of the compound is temporarily elevated to a higher level; it is said that the compound has effectively **absorbed a photon of light** (see section 1.1). After some time, the compound bounces back to its original, lower energy state, whereby it **emits a photon of light**.

Infrared light is the source of what we know as **heat (thermal) energy**. For instance, when we light a fireplace in our living room, it is not the convective currents of the warm air above the fireplace that is responsible for the heat produced in the room, but rather, it is the radiation of infrared light given off by the burning wooden logs that causes the room to heat up.

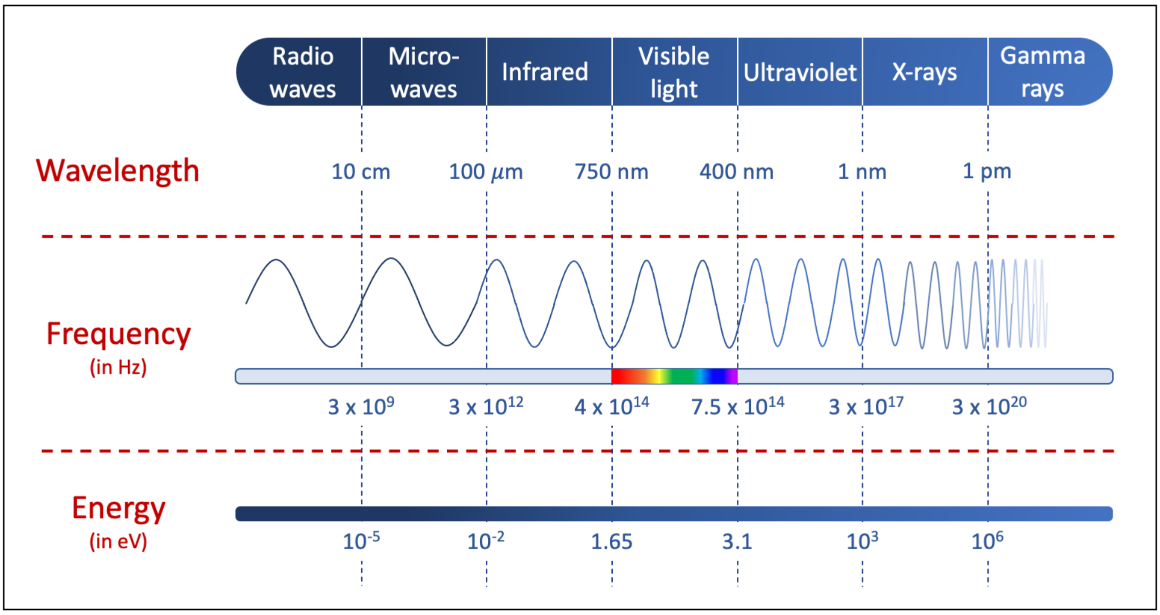


Figure 17.3: The electromagnetic spectrum of light

In the context of the **Sun-Earth system**, when the non-reflected portion of sunlight reaches the surface of the Earth, this incoming solar radiation is absorbed, i.e., the surface is heated, and then re-emitted in the form of infrared light (heat). Of that outgoing infrared light, about 60% finds its way back into space, whereas the remaining 40% is absorbed by both clouds and compounds in the atmosphere that are able to generate oscillating dipole moments and whereby the frequencies of the vibrational modes match the frequencies of infrared light—these compounds are often said to be **infrared active**.

As these compounds absorb the outgoing infrared radiation and re-emit it in all possible directions, some of that re-emitted heat radiation is redirected towards the surface of the Earth and contributes to further warming. In that sense, a part of the infrared radiation remains trapped within the atmosphere, continually taking part in the global warming of the Earth. This effect is designated as the **greenhouse effect**, and the atmospheric compounds that are able to absorb and re-emit infrared radiation are called **greenhouse gases, such as water (H_2O), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), ozone (O_3), and chlorofluorocarbons (CFCs)**.

Roughly speaking, the water vapour (H_2O) in the troposphere accounts for approximately half of the greenhouse effect (some claim up to 95%), whereas carbon dioxide (CO_2) and clouds each take up about 20%. The residual 10% is allocated to the other atmospheric gases.

With regard to the **carbon dioxide (CO_2)** compound, it is the *bending vibrational mode* of the O=C bonds that is most significant to the greenhouse effect, since the frequencies of this mode correspond with a specific range of frequencies within the band of infrared light of the electromagnetic spectrum that are most abundant in the atmosphere.

The compound **methane (CH_4)** does not have a net dipole moment in its resting state, similar to carbon dioxide (CO_2), but it has two vibrational modes in which it is infrared active. Moreover, despite having a much lower atmospheric concentration compared to carbon dioxide (CO_2), methane (CH_4) is a much more powerful greenhouse gas.

When it comes to **water (H_2O)**, the compound possesses a permanent dipole moment, making it therefore an important greenhouse gas as all of its vibrational modes are infrared active. If the temperature of the air rises, the greenhouse effect of water vapour (H_2O) becomes more pronounced because warm air is able to hold more water vapour (H_2O), and since water vapour (H_2O) is a greenhouse gas, more of it in the atmosphere further pushes the temperature up—this is called a **feedback effect**.

Nonetheless, even though water vapour (H_2O) is responsible for about half of the greenhouse effect, the compound carbon dioxide (CO_2) is more important in terms of climate change. That is, while water vapour (H_2O) can act as a feedback mechanism (e.g., if more greenhouse gases are added to the atmosphere, the temperature goes up, increasing the amount of water vapour in the air, which further rises the temperature and changes the climate), carbon dioxide (CO_2) is able to play the role of both a feedback system and **radiative forcing**, which means that adding it to the atmosphere (as is done through the human process of fossil-fuel burning (see section 13.1.4)) impacts climate change directly.

Put differently, carbon dioxide (CO_2) is an *active driver* of changes in the climate. In contrast, there are no known human or natural mechanisms, besides a change in temperature, for putting water vapour into the atmosphere in large enough quantities so that it *directly* impacts the climate—remember that the amount of water vapour in the atmosphere is variable due to evaporation and condensation processes.

Finally, bear in mind that **diatomic molecules**, which are made of two atoms of the same element, cannot cause any disturbances in the electrical field, because regardless of the amount of stretching and compressing of their bond, both atoms always pull at the bonding electrons with the same electrostatic force, i.e., they have the same electronegative value. Stated another way, diatomic molecules cannot create an oscillating dipole and do therefore not interact with the oscillating electromagnetic fields of light. In the context of the atmosphere, this means that both oxygen (O_2) and nitrogen gas (N_2), which are the main components of air (see section 17.1), can never be greenhouse gases.

17.3 Gaseous Pollutants

Gaseous pollutants, a.k.a. air pollutants, are generally taken to be gases or aerosols, i.e., minuscule solid particles or liquid droplets floating in the air, that originate from human-based activities and are harmful to the environment and living organisms. Some of the aerosols have a natural origin, such as sea salt particles and particles coming from erupting volcanoes and ravaging wildfires.

Human-produced **aerosols, often called particulates**, mainly stem from the burning of fossil fuels (see section 13.1.1), and, more specifically, they are predominately made of carbon (C) atoms as a result of the incomplete combustion of hydrocarbons (see Equation 13.3). These particulates form a threat to human health, since they can cause harm to the long tissue upon inhalation, potentially leading to lung diseases.

What is more, these aerosols impact the climate, as a larger number of them implies a greater amount of reflected sunlight as well as more cloud formation—in a nutshell, clouds are formed when water vapour condenses upon a tiny particle, such as an aerosol.

Apart from particulates, the combustion of fossil fuels (both complete and incomplete) also produce **the gaseous pollutants carbon monoxide (CO), carbon dioxide ($\mathbf{CO_2}$), sulphur dioxide ($\mathbf{SO_2}$), nitric oxide (NO), and nitrogen dioxide ($\mathbf{NO_2}$)—these two nitrogen oxides are jointly referred to as $\mathbf{NO_x}$**. The chemical equations for the production of carbon monoxide (CO) as well as carbon dioxide (CO_2) are explained in detail in section 13.1.4.

One of the most important impurities that are found in fossil fuels, especially in coal, is **sulphur (S)**. When these solid particles are exposed to high temperatures, they react with oxygen (O_2) to create sulphur dioxide (SO_2):

$$\mathrm{S}(s) + \mathrm{O_2}(g) \xrightarrow{\text{heat}} \mathrm{SO_2}(g) \tag{17.3}$$

Regarding the nitrogen oxides (NO_x), it is mostly the combustion of oil and coal that are responsible for their emission, with natural gas contributing only in a relatively small amount.

As **nitrogen (N)** atoms reside within the fossil fuels oil and gas, an exposure to high temperatures leads to the production of nitric oxide (NO), which further reacts with atmospheric oxygen (O_2) to create nitrogen dioxide (NO_2):

$$\begin{cases} \mathrm{N_2}(g) + \mathrm{O_2}(g) \xrightarrow{\text{heat}} 2\,\mathrm{NO}(g) \\ 2\,\mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{NO_2}(g) \end{cases} \tag{17.4}$$

When these gaseous pollutants are released in the atmosphere, they come into contact with water vapour (H_2O) and thereby form **acid rain**, which mainly consists of sulphuric acid (H_2SO_4) and nitric acid (HNO_3), with small traces of carbonic acid (H_2CO_3)—the chemical reactions for the formation of these acids are examined in detail in Equation 9.3.

Acid rain impacts the environment and human society in a number of ways. First and foremost, it leads to a growing **acidification of lakes**, which has already been reported, among other countries, in the United States, Norway, Canada, Sweden, and the United Kingdom. When the pH value gets too low (see definition 9.5), the natural environment becomes too acidic to support marine life, as in the case of trout, which is especially sensitive to overly acidic conditions.

Another concern is the **detrimental effect on soils, plants, and trees**. Although alkaline soils, which contain considerable amounts of limestone, i.e., calcium carbonate ($CaCO_3$), can (partially) neutralize acid rain, soils that are frozen, that consist mainly of sand, or that are poor in limestone, fail to neutralize the increasing acidity levels. One consequence of acidic soils is that they encourage the dissolution of aluminum ions (Al^{3+}) in wet environments (see Equation 17.5). These dissolved ions are toxic to plants and trees, as they slow down their growth by preventing the uptake of essential nutrients, such as calcium (Ca^{2+}).

$$2\,\mathrm{Al(OH)_3}(aq) + 3\,\mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{Al_2(SO_4)_3}(aq) + 6\,\mathrm{H_2O}(l) \tag{17.5}$$

Besides attacking trees from the bottom up, acid rain also causes them harm when small droplets gather on their leaves. That is, the acid rain steals away nutrients, such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and potassium (K^+) ions, at a pace faster than that at which the roots are able to make up for their loss. Trees that grow at higher altitudes, e.g., fir trees and spruce, are particularly at risk, because they are more exposed to clouds, which hold a greater amount of acidic rain compared to rain and snow.

Finally, acid rain not only corrodes metallic structures and vehicles (see Equation 14.9) but it also **erodes limestone rock**, which is often used in the construction of historical monuments, statues, and buildings, as well as in the processing of cement and asphalt concrete, since it converts limestone rock into the *soluble* salt calcium sulfate ($CaSO_4$):

$$\mathrm{CaCO_3}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{CaSO_4}(aq) + \mathrm{H_2CO_3}(aq) \tag{17.6}$$

17.4 Chlorine and Fluoride Ions in Drinking Water

Drinking water may contain a whole plethora of **contaminants**, such as physical contaminants (e.g., organic material or sediment), biological contaminants (e.g., parasites, bacteria, or viruses), radiological contaminants (e.g., elements with unstable nuclei, such as uranium, plutonium, and cesium), and chemical contaminants (e.g., toxins produced by bacteria, salts, bleach, metals, and pesticides, as well as arsenite (AsO_3^{3-}), arsenate (AsO_4^{3-}), fluoride (F^-), nitrate (NO_3^-), bromate (BrO_3^-), perchlorate (ClO_4^-), chlorate (ClO_3^-), and selenate (SeO_4^{2-}) ions).

With respect to the specific case of **fluoride (F^-)**, the specific concentration of this anion determines whether its presence in drinking water is beneficial or not. Purportedly, concentrations below 1.5–2.0 milligrams per liter ($mg \cdot L^{-1}$) of drinking water would have a protective function, particularly in children, against dental caries.

However, fluoride (F^-) concentrations above that threshold may trigger more adverse effects, such as dental fluorosis, i.e., tooth discolouration and weakening, and skeletal fluorosis, i.e., a weakening bone structure leading to impaired joint mobility and a higher likelihood of bone fractures.

In order to remove the many kinds of contaminants, drinking water undergoes a variety of treatments, including **screening** (i.e., the initial removal of large objects), **sedimentation** (i.e., small insoluble particles sink to the bottom of the water tank), **precipitation** (i.e., aqueous ions react with each other to form solids, which are subsequently removed; this stage is also known as *water softening*), **filtration** (i.e., precipitates that are too small to form sediments are removed by letting the water pass through a couple of layers, such as sand or gravel, that block these small particles), **adsorption** (i.e., dissolved organic compounds (chemical contaminants) attach to the surface of specially introduced substances, such as powdered activated carbon, which are then removed by filtration), and **disinfection** (i.e., the elimination of infectious biological contaminants).

Chlorine (Cl_2) and chloride compounds are often included in the drinking water treatment process, since they are effective disinfectants and kill off most of the pathogenic bacteria and viruses, such as legionella pneumophila, Escherichia Coli (E. coli), and salmonella typhi—this particular disinfection method is called *chlorination*:

$$Cl_2(g) + H_2O(l) \longrightarrow HClO(aq) + HCl(aq) \qquad (17.7)$$

In addition, as a *chemical oxidant*, chlorine (Cl_2) helps to get rid of the chemical contaminant arsenate (AsO_4^{3-}). Typically, it is more difficult to remove arsenite (AsO_3^{3-}) than arsenate (AsO_4^{3-}) from the water, so chlorine (Cl_2) is used to first oxidize arsenite (AsO_3^{3-}) into arsenate (AsO_4^{3-}), which is then removed.

However, concerns exist about some of the by-products of chlorination, such as the carcinogenic trihalomethanes, which is why chlorine (Cl_2) is often replaced by **chloramines**, e.g., monochloramine (NH_2Cl) and dichloramine ($NHCl_2$).

Finally, to aid the treatment process of sedimentation for solid impurities that have too little mass to sink, a substance called a *coagulant* may be added to the water. The coagulant forms a solid precipitate that traps these impurities within its structure, making the entire solid compound heavy enough to sink. A chloride compound called ferrite chloride ($FeCl_3$) is sometimes used as a coagulant for this process designated as **coagulation**:

$$2\,\mathrm{FeCl_3}(aq) + 3\,\mathrm{Ca(OH)_2}(aq) \longrightarrow 2\,\mathrm{Fe(OH)_3}(s) + 3\,\mathrm{CaCl_2}(aq) \tag{17.8}$$