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Chemistry for Chemical Engineers

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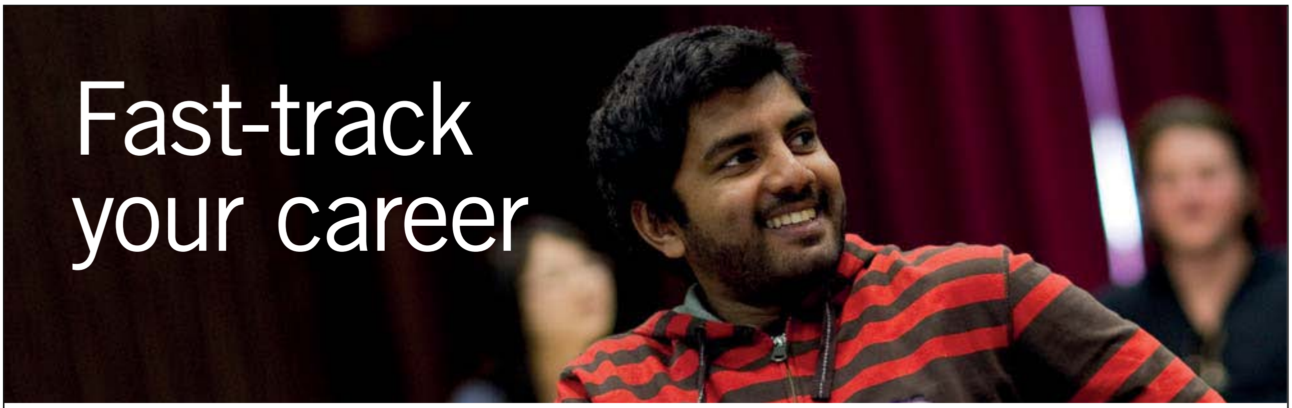


Two of the main distinctions between chemical engineers and other engineering disciplines are the topics of mass and energy balances. Within these two topics there are a lot of underlying chemical principles that help chemical engineers to perform calculations to determine what is happening in a system, allowing better control of a process.

This book will outline the basic chemistry principles that are required by chemical engineers to understand chemical reactions and relate them to the main themes of mass and energy balances. It does not serve as a complete account of all the chemistry that is important for chemical engineering but should give a grounding, which can be supplemented by reading further into the areas discussed, if required.

Quantifying systems

Working as a chemical engineer requires a capacity to interpret data and quantities provided from different sources. It is essential that any quantities used or calculated are recorded correctly, as the inclusion or omission of units changes the context dramatically. For example 7 is a purely numerical quantity, but adding a unit, say kilograms so the measurement becomes 7 kg, conveys significantly more information. In all working it is important to write down both numerical values and the corresponding units; as a result, it is necessary to appreciate the relationship between certain units and have an ability to convert between quantities. The properties that can be measured, such as time, length and mass, are known as dimensions and can also be composed from multiplying or dividing other dimensions, for example velocity (length/time). Units can be treated like algebraic variables when quantities are added, subtracted, multiplied or divided but note that numerical values may only be added or subtracted if their units are the same. The most common set of units that chemical engineers come into contact with are the seven fundamental S.I. units of measurement, as defined in the International System of Units (the abbreviation S.I. comes from the French for this classification: *Système Internationale d'Unités*). The system was developed in 1960 and has been widely accepted by the science and engineering communities.

The table below shows the seven base units and their corresponding abbreviations, as chemical engineers the most commonly used units will be those for amount of substance, mass, length, temperature and, importantly, time.

Property	Unit	Abbreviated Notation
amount of substance	Mole	mol
electric current	Ampere	A
Length	Metre	m
luminous intensity	Candela	cd
Mass	Kilogram	kg
temperature	Kelvin	K
Time	Second	s

Base units of measurement according to the S.I. classification

The seven units within the S.I. are referred to as ***base units***, so for length that would be metre (m), but these can be converted to other systems of measurement that represent the equivalent dimension, such alternative units are referred also known as base units but not S.I., so for the example of length one could use (ft).

Sometimes, quantities are calculated from several dimensions, this is very common in chemical engineering where flowrates, such as mass or volumetric flowrate are frequently used. In this case the quantities are measured as mass/time (kg/s) and volume/time (m^3/s); the corresponding units are a composition of all the dimensions involved and are known as ***derived units***.

Common derived units are listed in the table below. It should be noted that these dimensions have their own unit and abbreviated notation, in addition to that from their derivation.

Equivalent property	Unit	Abbreviated notation	S.I. derived units
Volume	litre	l or L	0.001 m^3 or 1000 cm^3
Force	Newton	N	1 kg m/s^2
Energy	kilojoule	kJ	10^3 N m
Pressure	bar	Bar	10^5 N/m^2
Power	kilowatt	kW	1 kJ/s

Commonly used derived units

Note 1 N is defined as being equivalent to 1 kg m/s^2 because a force of 1 N produces an acceleration of 1 m/s^2 when applied to a mass of 1 kg. It is, therefore, useful to remember that 1J ≡ 1 N m ≡ 1kg m^2 s^{-2} in order to simplify complex units generated in some equations.

The base units are not always the most useful mathematical representation of the numerical value determined and may be necessary to use other methods to simplify the quantity. For example, 60 s can be represented as 1 minute (1 min), similarly 0.000001 s could be represented as 10^{-6} s or 1 μs, the latter unit (microseconds) and min are known as ***multiple units,*** and it is essential to be able to understand not only the quantities involved in a system but also their level of scale. Chemical engineers must be comfortable with the common prefixes used with S.I. units and other units from around the globe. Commonly used prefixes are given below, with their names and numerical value.

Tera	(T)	10^{12}	pico	(p)	10^{-12}
Giga	(G)	10^9	nano	(n)	10^{-9}
mega	(M)	10^6	micro	(μ)	10^{-6}
Kilo	(k)	10^3	milli	(m)	10^{-3}
			centi	(c)	10^{-2}
			deci	(d)	10^{-1}

Common prefixes in metric system

Converting units is an essential skill for all chemical engineers and the easiest method to use is fractional representation. This keeps track of all numerical values and units throughout the conversion performed, allowing those units that cancel to be easily identified.

The equivalence between two expressions of a given quantity may be defined in terms of a ratio (expressed here in common fraction notation):

$$\frac{1\,\mathrm{cm}}{10\,\mathrm{mm}}$$ 1 centimetre per 10 millimetres

Ratios of this form are called ***conversion factors***. Generally, when converting units, multiply by conversion factor(s) as fractions with new units as the numerator (top) and old units as the denominator (bottom). For example, convert 100 mm into cm:

$$100mm \times \frac{1cm}{10mm} = 10cm$$

Worked example – convert the gas constant from 8.314 J mol^{-1} K^{-1} to Btu lb-mol^{-1} $^{o}C^{-1}$, using the following conversions:

1 kJ = 0.9478 Btu; 1 kmol = 2.205 lb-mol; 1 K = 1 ^{o}C

Firstly, write out the value given in fractional format: $\frac{8.314\,\mathrm{J}}{\mathrm{mol\,K}}$

Then write out each of the required conversions in the same format, making sure that the units match and can cancel out in the working. For example, if the value to be converted has J on the top line, and the conversion of 1 kJ = 0.9478 Btu is to be applied, it is firstly required that J is converted to kJ. To do this, divide through by 1000 J and multiplying by kJ (as 1 kJ = 10^3 J = 1000 J). After this, kJ is now on the top line:

$$\frac{8.314\,\mathrm{J}}{\mathrm{mol\,K}} \times \frac{1\,\mathrm{kJ}}{1000\,\mathrm{J}} = 8.314 \frac{\mathrm{kJ}}{1000\,\mathrm{mol\,K}}$$

It is then possible to use the conversion, 1 kJ = 0.9478 Btu, directly, to arrive at:

$$8.314 \frac{\mathrm{kJ}}{1000\,\mathrm{mol\,K}} \times \frac{0.9478\,\mathrm{Btu}}{1\,\mathrm{kJ}} = 8.314 \frac{0.9478\,\mathrm{Btu}}{1000\,\mathrm{mol\,K}}$$

Building up the conversions over the whole set of units to be converted produces:

$$\frac{8.314\ \text{J}}{\text{mol K}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{0.9478\ \text{Btu}}{1\ \text{kJ}} \times \frac{1000\ \text{mol}}{1\ \text{kmol}} \times \frac{1\ \text{kmol}}{2.205\ \text{lb - mol}} \times \frac{1\ \text{K}}{1^{\circ}\text{C}} = 3.573\frac{\text{Btu}}{\text{lb} - \text{mol}\ ^{\circ}\text{R}}$$

Extreme care must be taken when converting squared and cubed dimensions, remember that not only the numerical value needs to be squared or cubed, the units must be treated in the same way. For example, converting 0.6 m^3 to ft^3, using the conversion 1m = 3.281 ft, requires that the fractional conversion is applied and cubed in its entirety. It is important to note that all four terms in the conversion must then be cubed in the expanded form:

$$1\,\text{m}^3 \times \left(\frac{3.281\ \text{ft}}{1\ \text{m}}\right)^3 = 1\,\text{m}^3 \times \frac{(3.281)^3 \cdot (\text{ft})^3}{(1)^3 \cdot (\text{m})^3} = 1\,\text{m}^3 \times \frac{35.3198\ \text{ft}^3}{1\,\text{m}^3} = 35.3\ \text{m}^3$$

Atoms and bonding

Understanding atomic and molecular structure is essential in determining several reaction parameters and provides chemical engineers with a deeper insight into the mechanics behind the process being controlled or scaled-up. This knowledge also provides a common language for use with scientists and engineers from other disciplines ensuring everyone follows a discussion or document fully. There are several particles and modes of reaction chemistry that require definition.

The atom

Atoms are basic building blocks of chemical structures; the Greek name means indivisible suggesting their role as base chemical building blocks. They consist of a dense nucleus (containing over 99% of the mass), generally composed of protons and neutrons, which is surrounded by an electron cloud. Protons are positively charged, neutrons are, as their name somewhat suggests, neutral and electrons carry a negative charge. Electromagnetic forces, involving the charged species, bind the electron cloud to the nucleus. Similar attractions bind atoms to each other to produce molecules.

Atoms are small, low weight, neutral species, unless they have undergone addition or loss of electrons to produce negatively or positively, respectively, charged atoms known as ions. Elements consist of atoms of only one type, and an element is defined as matter that cannot be broken down further by chemical methods. Each element can be identified by the number of protons and neutrons contained in the nucleus; the number of protons governs the element and the number of neutrons dictates which isotope of the element is being studied.

The concept of atoms being indivisible has existed for centuries and is related to the law of conservation of mass, but in the late 1800's to early 1900's, this idea was replaced by that of the existence of subatomic particles, such as the electron discovered by J.J. Johnson, which became the subject of much research. The atom was no longer unable to be broken down, as defines an element, but it was by physics rather than chemistry that this was discovered. The nucleus, as a dense positive mass, was proposed by Ernest Rutherford as a result of experiments using alpha rays (positive helium ions) to bombard gold foil

Atomic theory was developed in the early 19th century, when John Dalton used atoms as the rationale for the way elements react in specific proportions, i.e. small whole numbers, and the reason that some gases dissolve better in water; postulating that elements are composed of small units called atoms and these react to produce larger chemical species. This hypothesis was built on, and eventually verified, over the years with evidence including the determination of the size of atoms, the discovery of Brownian motion and a combination of theoretical and experimental methods to measure the mass and physical dimensions of atoms.

J.J. Johnson proposed a model based on a cloud of electrons, with a balancing positive cloud, however Rutherford's work disproved this theory. Consequently Niels Bohr suggested that electrons are in fact confined in well defined, quantised orbits, between which electronic transitions can occur by the absorption or emission of specific, quantised packets of energy. This refined the atomic model to the point where it was accepted that atomic number is equal to the atomic nuclear charge of a given element. The atom consists of a number of sub particles and units.

Nucleus – The components of a nucleus, proton and neutrons, collectively called nucleons, are held together by the strong forces associated with gluons, an elementary particle. The nucleons are bound together by the short-ranged residual strong force, which is an attractive potential and exceeds that lesser electrostatic repulsion of like charged particles. By overcoming the binding energy of the nucleus, nucleons may be lost from the atom forming an isotope, discussed in more detail later. The number of protons in the nucleus determines the element and this value is known as the atomic number, the number of neutrons determines the isotope of the given element. The total number of nucleons determines the nuclide. Some nuclei may then become unstable and be subject to radioactive decay. The energetics of the nucleus are complex with protons and neutrons being unable to occupy the same quantum physical state as their own type as described by the Pauli Exclusion Principle. Generally, atoms with low atomic numbers are most stable when they have similar numbers of protons and neutrons. For heavier atoms the electrostatic repulsion of the increasing number of protons requires more neutrons to maintain stability, tending towards a ratio of 1.5.

Protons – With a mass of 1.6726×10^{-27} kg ($1836 \times m_e$), ignoring binding energy changes, protons have dimensions of approximately 2.5×10^{-15} m and carry a positive charge equal in magnitude to an electron. Protons themselves contain the smaller basic units called quarks, which are one of the second smaller basic components of matter, known as fermions. They contain two up quarks ($+\frac{2}{3}$) and one down quark ($-\frac{1}{3}$) giving a net charge of +1.

Neutrons – With comparable dimensions to protons, neutrons are marginally greater in mass at 1.6929×10^{-27} kg. They have no electrical charge and are, like protons, composed of quarks, in this case one up quark ($+\frac{2}{3}$) and two down quarks ($-\frac{1}{3}$), giving a net charge of 0.

Electrons – The particle with the least mass ($m_e = 9.11 \times 10^{-31}$ kg), the electron is negatively charged and too small to be measured by current experimental methods. The electron is an example of a lepton – one of the basic components of matter. Electrons are bound to the nucleus by electromagnetic forces and control the chemistry of the element, influencing the reactivity and bonding. In order for an electron to be lost from the atom, external energy is required, proportional to the energy binding the electron to the nucleus, and is significantly less than the binding energy of the nucleus itself. The energy needed for electron loss increases the closer the electron is to the nucleus. If an atom has the same number of protons and electrons, the charges balance and the atom is said to be neutral. An inequality, with either an excess or deficit of electrons, results in a charged atom, known as an ion.

Atomic properties

Due to the structure of atomic orbitals, atoms may lack a defined shape so the atomic radius, the distance to which the electron cloud extends from the nucleus, is used to define their size and is often calculated from the distance between two atoms joined in a chemical bond. This has limitations as it assumes a perfectly spherical shape, and is dependent on the type of bond and the number of neighbouring atoms.

Atoms, as stated above, are composed of smaller particles and this discovery caused myriad models to be proposed regarding the interaction of these particles with those of other atoms. Such models include Thomson's *plum pudding model*, which stated electrons orbited a jelly-like positive matter in rings akin to the planets orbiting the sun. Shortly thereafter Nagaoka proposed a model where a dense central positive core attracted the electrons into orbiting rings, similar to the rings of Saturn. This model has a major flaw in that, classically, charged objects have no means of sustaining an orbit due to radiative energy loss through acceleration. However, Nagaoka was a lot closer than any of his contemporaries and eventually the Bohr model was developed.

Rutherford determined that the positive mass of an atom exists in the densely packed nucleus, eliminating a number of models, including the plum pudding model. On the basis of this, Bohr suggested a model where the nucleus was orbited by electrons contained in discrete shells but where the electrons could only take specific angular momentum values; this addressed the issue of energy loss. By setting conditions for electrons to satisfy, this also explained the quantised spectral lines obtained in absorption and emission spectra of atomic species. The wavelength associated with the energy loss or gain gave weight to the theory electrons behave like waves and, eventually, the concept of wave/particle duality.

Many particles, including electrons, possess the properties of both a particle and a wave, in the case of an electron meaning that the particle forms a three-dimensional standing wave in the potential well created by the forces between the nucleus and electron. This standing wave has no relative movement with respect to the nucleus and is defined by an atomic orbital, mathematically representing the probability of the location of an electron at the time of measurement. These atomic orbitals are well defined and only exist in specific forms that are the most stable orbitals, with a range of nodes, shapes, sizes and orientations. The concept of electrons acting as waves allows their behaviour to be accurately described by quantum mechanical theory and limiting criteria such as the Pauli exclusion principle, which is related to spin of electrons in a given orbital, and Hund's rule of maximum multiplicity, a maximum of two electrons with opposite spin may occupy one orbital, as well as giving rise to phenomena such as the Heisenberg uncertainty principle, which states that a particles such as electrons would require infinite angular momentum in order to occupy a specific geometric position in space since their wave function is based on a frequency distribution.

To exist in a given atomic orbital, the electron must have a specific energy particular to that orbital, energy gain or loss can move electrons between orbitals. Such energy changes are provided by the absorption or emission of a photon, the energy of which can be interpreted to give information about the atom studied. Each atomic orbital has a specific set of characteristics that must be satisfied for an electronic transition to be permitted. These characteristics are the angular momentum (l), angular momentum direction (m) and energy (n) of the orbital. The orbitals have letters: s, p, d and f ($l = 0$, 1, 2 and 3, respectively) indicating their shape and electronic configurations. The names derive from the characteristic spectroscopic lines observed for each orbital: sharp, principal, diffuse and fundamental. g-orbitals are ignored herein for simplification as they will not be necessary for most chemistry covered within a chemical engineering degree.

The complete electron cloud for an atom is, approximately, a summation of all these orbitals, where electrons are paired and arranged, according to energy (n) and angular momentum (m), in sets of repeating units of incrementally increasing odd integers: 1, 3, 5, 7 (s, p, d and f, related to l), which explains the repeating periodicity of 2, 6, 10 and 14 elements in the periodic table. The fact that elements in the same group exhibit similar chemical properties was not fully understood at first using the Bohr model but each group of orbitals holds different numbers of electrons giving similar outer shell valences for members of the same group even though they differ markedly in electron number. This is related to the existence of groups of atomic orbitals.

s-orbitals – exist as singular orbitals and are spherically shaped, here $l = 0$. If the energy level is 1, i.e. $n = 1$, then this orbital is very dense at the centre, fading exponentially towards the outer edge, it is approximately solid. For $n = 2$ and higher there exist spherically symmetric surfaces as an array of nested shells. All s-orbitals have an anti-node at their radial centre, which is a region of high wave function density and is at the centre of the nucleus. As the other three types of orbitals (p, d and f) possess angular momentum they avoid the nucleus, consequently having a wave node at the nucleus in contrast.

p-orbitals – are present from $n = 2$ upwards and are elliptical in shape, consisting of three pairs of ellipses that have a point of tangency at the nucleus, hence the wave node, and resemble a trio of dumbbells. The three orbitals are oriented along the three (x, y, z) axes and may be individually referred to as p_x, p_y and p_z.

d-orbitals – are present from $n = 3$ and in keeping with the $2x$-1 series within the orbitals have 5 wave functions in ψ^2 form. Four of these are similar with two pairs of ellipses, like the p-orbitals each, such that each of the four d-orbitals have 4 lobes. They lie along the xy, xz, yz and the fourth has centres on both x and y axes, and are referred to as d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$. The fifth d-orbital consists of a single pair of ellipses along the z-axis, with a torus, a doughnut shaped ring, around their centre, it is known as d_{z^2}.

It is evident that the complexity of the orbitals increases along the series and the f-orbitals and g-orbitals are too complex to describe here. It is sufficient to know that there are seven f-orbitals (f_{z^3}, f_{xz^2}, f_{yz^2}, f_{xyz}, $f_{z(x^2-y^2)}$, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$) and that they are present from $n = 4$.

The electrons furthest from the nucleus, i.e. in the outermost orbitals, can be shared by or transferred to other atoms to allow the formation of molecules and other chemical species via bonds.

Molecular orbitals

Similar to the way that atomic orbitals (AOs) describe the wave function of an electron in an atom, molecular orbitals (or MOs) are mathematical functions that describe the behaviour of electrons within molecules. As such, MOs are usually formed by the combination of AOs, or in some cases hybrid orbitals, from each atom in the molecule and the overall MO can be used to predict chemical and physical characteristics. The use of atomic orbitals to represent MOs is called the linear combination of atomic orbitals (LCAO-MO) method.

MOs are essentially Schrödinger orbitals with more than one, but often only two, nuclei. The actual formation of a MO is governed by the symmetries of the AOs and whether this is allowed can be determined using group theory. It should be noted that the number of MOs formed should be the same as the number of AOs combining to form them.

There are a variety of MOs that can form, these being bonding, anti-bonding and non-bonding MOs.

Bonding MOs – Bonding MOs have lower energies than the combined AOs used to produce them, the bonding interactions between the AOs are constructive. Bonding MOs have within them electrons with a higher probability of being found between the nuclei than any other location in the molecule, tending to hold the nuclei, hence, the molecule together. Thus they are referred to as bonding MOs.

Anti-bonding MOs – Anti-bonding MOs have higher energies than the combined AOs used to produce them, the bonding interactions between the AOs are destructive. Anti-bonding MOs have within them electrons with a higher probability of being found at any location in the molecule other than between the nuclei, tending to weaken the interaction between the nuclei, hence, the molecule. Thus they are referred to as anti-bonding MOs.

Non-bonding MOs – Non-bonding MOs have the same energy as the AOs of one of the atoms in the molecule, there are no bonding interactions between the AOs, usually as a result of incompatible symmetries. Non-bonding MOs tend to be deep, almost atomic, orbitals and, as such electrons tend to be associated with one nucleus or another, neither strengthening nor weakening the bond.

HOMO and LUMO – the difference in energy of individual electrons within a molecule can be a useful quantity to determine and is called the band gap, and gives an indication of how easily excited a molecule is, which has applications in semiconductor development. The band gap relates the energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Bond symmetry

The interactions that occur when AOs are combined can be categorised into either sigma (σ) or pi (π) symmetries. σ -symmetry MOs are the result of the interaction of two s-AOs or two p_z-AOs, and occur if the orbital and axis joining the two AOs are symmetrical with respect to each other, this is called the internuclear axis, and rotation about this axis does not result in a phase change, this lack of phase change on rotation is also the case for σ* MOs (sigma antibonding). π -symmetry MOs are the result of the interaction of two p_x-AOs or two p_y-AOs, and occur if the orbital and internuclear axis are asymmetrical, i.e. rotation about this axis causes a phase change. Similarly, rotation of a π* MO about the internuclear axis will also produce a phase change.

Molecular Orbital (MO) theory

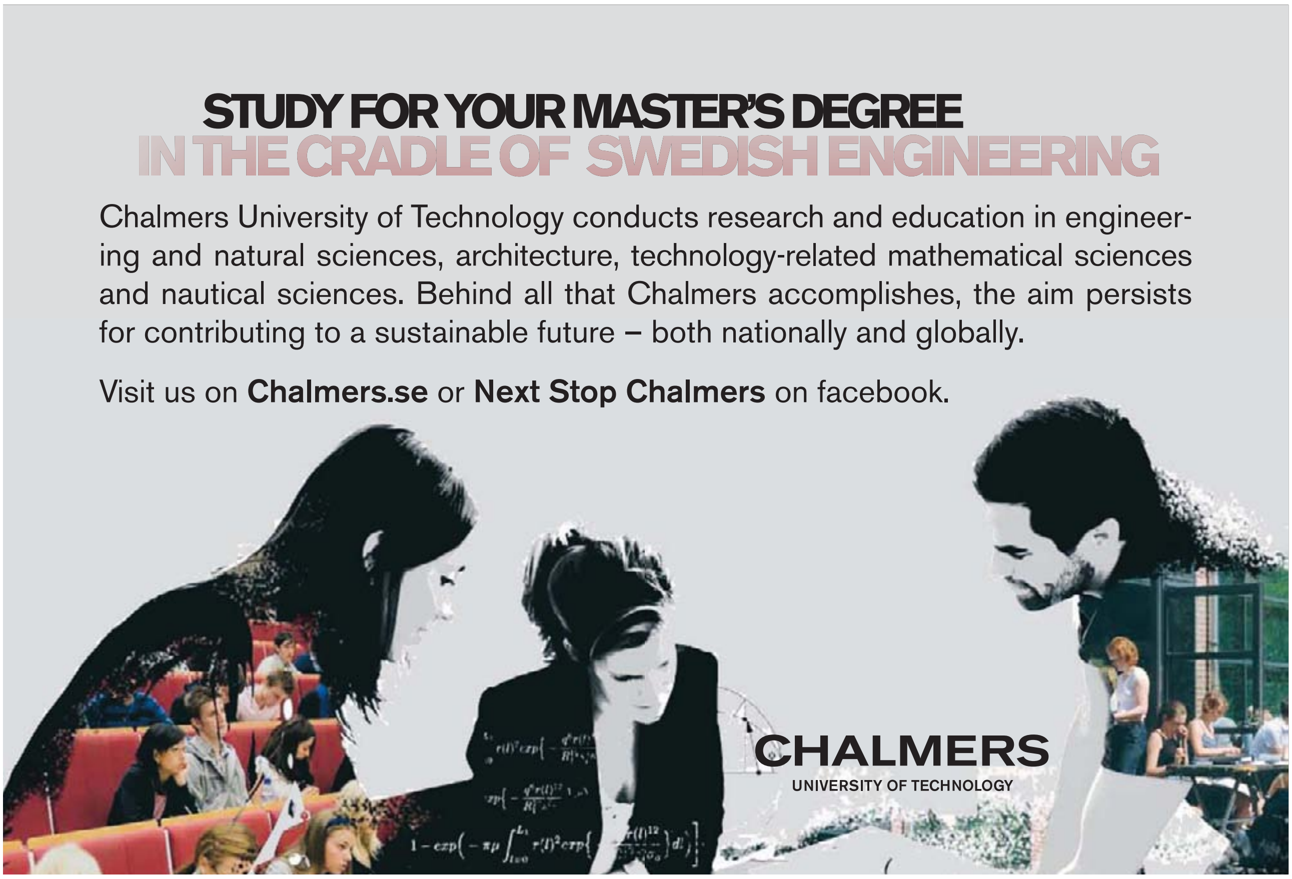
Molecular Orbital (MO) theory allows the determination of molecular structure where electrons are not assigned to specific bonds between selected atoms, but are allowed to move within the whole molecule as a result of interactions with the atoms' nuclei. Molecules each have MOs as described above, and any electron, of that molecule, may be located anywhere in that molecule. These electrons may by more associated with one nuclei than another or be spread fairly uniformly over the molecule in MO theory meaning it is useful when considering extended systems.

MO diagrams – It is possible to visually represent the bonding interactions within a molecule using molecular orbital (MO) diagrams. Within such representations, horizontal lines denote MOs and the higher the line from the base of the diagram, the higher the energy of the orbital. Degenerate (or equal energy MOs) are placed at the same height with a small space between each MO line. Once all MOs have been added to the diagram, the electrons are added individually, ensuring that the Pauli exclusion principle and Hund's rule of maximum multiplicity are obeyed such that single electrons are added to all MOs in one level before pairing and moving on to the next set of MOs. There are exceptions and more complicated systems within such diagrams, but these are not considered here.

Valence bond (VB) theory

Valence bond theory is the idea that a bond forms when two valence electrons, those electrons able to take part on bonding, have the role of holding two nuclei together by lowering their relative energies. Linus Pauling was influential in the development of this field establishing six key rules for bonding:

1) Each atom in the electron pair bond formation contributes one unpaired electron
2) These electrons must have opposing spins
3) These electrons, once paired, may not participate in any further bond formation(s)
4) There is only one wave function per atom involved in the electron exchange terms
5) The strongest bonds are formed by electrons in the lowest available energy levels
6) Orbitals that can overlap most form the strongest bonds and the bond forms lies in the direction of the summative orbital.



Comparison of VB and MO theory

The two methods are similar, becoming equivalent once extended, and are essentially both approximations of the alternative quantum theory, which is often used to predict the behaviour of molecular species. There are marked differences between the two approaches, for example in hypervalent molecules, where main group species can have greater than eight electrons in their outer shells, d-orbitals are essentially ignored in MO theory, whereas they play a crucial role in VB. Each has its strengths, for example VB theory provides a far superior approximation for the hydrogen molecule, and MO theory is more useful in predicting molecular spectroscopic, magnetic and ionisation properties.

Intermolecular interactions

Many bonding interactions and molecular forces can be attributed to a range of intermolecular forces. In order increasing strength they are:

London dispersion forces (0–25 kJmol^{-1}) are the result of the influence of neighbouring atoms on each other, as their electron clouds will not be uniform and their orientation with respect to their neighbours can induce a non-permanent dipole as a consequence.

Dipole-dipole interactions (0–50 kJmol^{-1})are the result of dipoles that can be induced on atoms or molecules as a result of differences in relative electronegativity of system species or electron transfer, the former produce partial charges and the latter give rise to more permanent charges.

Cation-pi interaction (5–80 kJmol^{-1}) is the interaction of a cation, positively charged, and the negatively charged electron density associated with an aromatic ring.

Hydrogen bonding (4–120 kJmol^{-1}) is essentially the result of a large difference in electronegativites between hydrogen and the atom to which it is bonded, producing a fixed dipole that causes strong electrostatic interactions. In water, the interactions between molecules raises the boiling point of water above that expected.

Bonding types and characteristics of bonds

The attractions between atoms that allows them to form larger structures, called molecules, are known as chemical bonds. These bonds involve electrostatic interactions of varying strengths and can be the result of electromagnetic force attractions between formal charges, such as electrons and nuclei, or dipole interactions. Chemical bonds vary in strength from ***strong bonds***, such as covalent or ionic bonds, to ***weak bonds***, such as dipole-dipole interactions, hydrogen bonding or London dispersion forces.

In the case of a bond forming as the result of an interaction between formal charges, negatively charged electrons will be attracted to positively charged protons in the nucleus. As two atoms participating in a bond will each have a nucleus, the electron will be attracted to each, hence, the most stable configuration of the three particles is for the electron to spend most of its time between the two nuclei than anywhere else in the atom spaces. The result is that the two nuclei are attracted to each other, forming a bond. The nuclei do not approach each other to become indistinguishably close as the wave character of the electrons means that they occupy a volume far greater than their mass dictates, keeping the nuclei separated. Strong bonds are normally associated with such sharing of electrons between atoms and are often ***covalent bonds***, known as electron sharing bonds, as the electrons are equally shared in the overlapping electron space between the atoms involved in the bond. There is an exception to this in the polar covalent bond, where the electrons are shared unequally giving rise to polar characteristics to the bond. Covalently bonded species are often Lewis acids and bases (see chapter on Acids and Bases), which can accept or donate electron pairs, respectively, such chemistry is important in ligand and chelating applications.

Ionic bonds do not involve sharing of electrons; rather the bonding electron is transferred to one of the atoms, which is generally dictated by the ***electronegativity*** of the elements involved. Electronegativity is the ability of an element to attract electrons to itself, and there are large differences in electronegativity between the atoms involved in ionic bonds. Ionic bonds involve at least one atom with an outer orbital vacancy that is able to accept the donation of electron from another atom. Often these electrons will occupy lower energy orbitals and experience closer interaction with nuclei than in their original atoms, allowing transference of the electron to the second atom. The movement of an electron from one atom to the other produces a net positive charge on the atom losing the electron, and a net negative charge on the atom gaining an electron. The magnitude of the charge can increase with increasing numbers of electrons lost or gained. The resulting charged species are known as ***ions***.

There is a final class of bonding called ***metallic bonds***, where electrostatic forces exist between delocalised electrons and positively charged metal ions. It is easiest to think of this model as a set of metal cations in a 'sea of electrons', this gives rise to the conductive nature of many metals. It should be appreciated that this type of bonding is over a whole, rather than singular atomistic species.

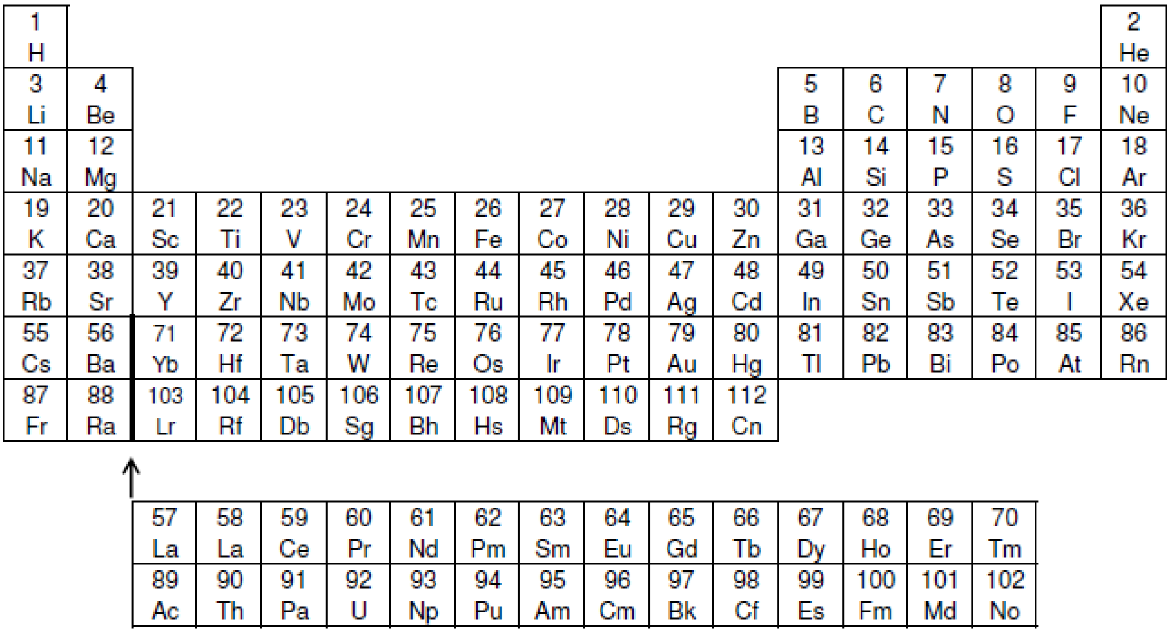
Bond order – this is related to the number of electrons in bonding and anti-bonding orbitals, such that bond order = 0.5 x [(number of electrons in bonding MOs) – (number of electrons in anti-bonding MOs). This is due to the fact that the bonding and antibonding electrons cancel each other out and the remaining electrons are paired.

Bond length – this is inversely proportional to bond order and represents the distance between the nuclei of bonded atoms.

The periodic table

Organising the elements

All substances and materials are composed of one or more of the fundamental states of matter known as the elements. There have been many attempts to categorise and group the elements into families of similar materials, with the eventual development of the precursor of the current periodic table, as proposed by Dmitri Mendeleev in 1869. Only elements are grouped in the table and this format collects the elements into seven periods (the horizontal rows) and 32 groups (the vertical columns) and is a visual version of the periodic law, by which elements show periodic repetition of chemical properties in correlation with their atomic number. The periodic table, in this format, includes gaps in the horizontal rows to ensure chemically similar elements are grouped accordingly. Some of the groups have assigned names, such as alkali metals, alkali earth metals, halogens and noble gases. Some periods also have special names, including the transition metals, actinides and lanthanides; It is worth noting that most modern periodic tables will show only 18 groups, this is due to the removal of the lanthanides and actinides, referred to as the f-block, into a separate block of two rows often shown below the main table and unnumbered, which allows simplification of the table.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	71 Yb	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn						

57 La	58 La	59 Ce	60 Pr	61 Nd	62 Pm	63 Sm	64 Eu	65 Gd	66 Tb	67 Dy	68 Ho	69 Er	70 Tm
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

The periodic table of the elements

As the elements are grouped by chemical nature, this allowed the properties of many elements to be predicted before the element had even been discovered. The elements up to atomic number 112 have been isolated in nature to varying degrees, 91 of these being considered primordial elements, while those with atomic number 113 and above have only been produced in the laboratory. The elements are often named after those who discovered them or something pertinent to their providence or the discoverer; the formal procedure of adopting names for the elements falls to IUPAC (the International Union of Pure and Applied Chemistry).

The recurring chemical nature of the elements is ascribed, by quantum mechanical theories, to the configuration of electrons within atoms, with each period corresponding to an electron shell. As the number of electrons in the shell increases, the periods become longer.

The table shown deals only with the naturally isolated elements. In this modern version of the periodic table, all of the known elements are arranged in order of their atomic number, from left to right across the periods, Each new period starts with the next atomic number after the last element listed in the previous row and there are no gaps or duplication, as the masses given are the average of the atomic masses for all known isotopes in their relative proportions. It is worth noting here that the atomic masses do not always increase incrementally with atomic number so preceding elements may be lighter than their neighbours, due to the numbers of neutrons in the nuclei of isotopes and isotopic proportions.

Periodic table groups

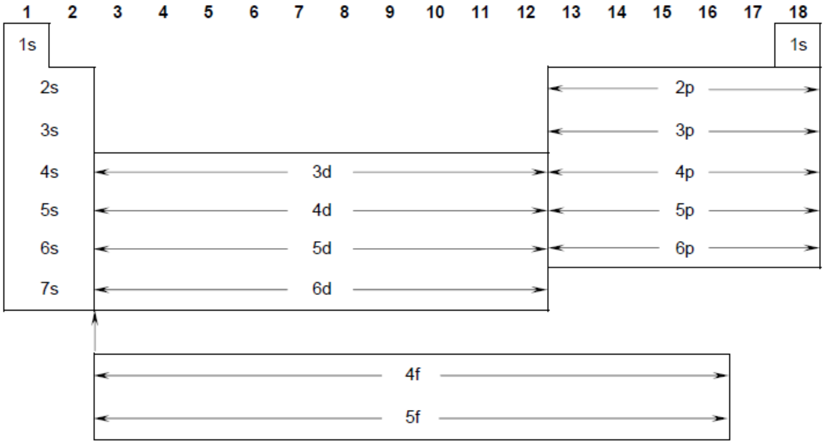
The vertical columns of the periodic table are also called groups and this grouping of elements with similar electronic structure is important in predicting reactivity and structure of substances composed of certain elements as well as for the elements themselves. Some groups, for example group 8, the noble gases, exhibit very similar properties within the group. The groups are numbered 1 through 18 starting from the left-hand most column. Properties that are exhibit trends within groups are the atomic radii, electronegativities and ionisation energies. Descending down a group the atomic radii increases, as a result of the increased distance that the outer electrons can be found from the nuclei as more shells are filled with increasing atomic number. Again, descending the group, decreases the electronegativity of the elements as the distance between the nucleus and outer electrons increases, similarly the ionisation energy decreases moving down the group as electrons become easier to remove as a consequence of them being further from the nucleus.

Periodic table periods

The horizontal rows of the periodic table are known as periods, and are much less used to classify trends in elements, however, there are groups, such as the transition metals, part of the d-block, where such horizontal groupings are useful in describing the expected chemistry of the elements. The lanthanides and actinides are two further cases, known as the f-block, which are shown as separate horizontal groups in the periodic table above. Ionisation energy also trends within the periods, as may be expected; the value decreases moving across the period from left to right as a result of the increasing distance of the outer electrons from the nucleus. Other properties trending across periods include atomic radii, usually decreasing as subsequent shells fill, and electronegativity, increasing for the same reasons as ionisation energy decreases.

Due to the inherent chemical properties associated with the different sections of the periodic table, many people refer to them as the periodic table blocks, and their respective names, and often chemistry, is derived from the shell containing their outermost electron(s). Hence, there are four key recognised zones, that are named after the outermost electronic shell containing electrons, and these are known as the s-block, p-block, d-block and f-block.

Periodic table blocks



The periodic table of the elements showing table blocks

Main group elements

The main group elements include those with s and p outershell electrons, i.e. those in the s- and p-blocks. These elements are the most abundant in the Earth's composition and within the Universe, and may also be referred to as the representative elements.

Electronic configurations

Electronic configurations can be used to show the occupation of orbitals and subshells for a given element, allowing the reader to understand their potential for bonding and reaction. The method use to write electronic configurations uses a combination of s, p, d and f notation and numbers.

It is easiest to build up an understanding of how to write electronic configurations by starting with the simplest atoms and increasing the level of complexity over a number of elements with sequentially increasing electron count. This can be done by starting with the first period of the table.

The first element in the first period is hydrogen, with one electron, which is located in the 1 s orbital as this has the lowest energy of all the orbitals. Hence, the electronic configuration is written: $1s^1$. The second element, helium has 2 electrons, again located in the 1s orbital; as the first shell consists of only an s orbital coupled with the fact that s orbitals can only accommodate 2 electrons, this completes the filling of the first shell. The electronic configuration is hence $1s^2$.

As the first shell is now full, any additional electrons will need to be accommodated in higher energy shells and their orbitals, starting with the second level with progression into the second period. The next element is lithium with 3 electrons. The first two fill as for helium, i.e. $1s^2$, then the third electron is located in 2s, as this is the next lowest energy level, hence the electronic configuration is written $1s^2$ $2s^2$, note that there are no commas between the shells, nor between orbitals in shells, it is all written as one string of text. As you may be aware, each of the noble gases will complete the filling of a shell, hence their inert behaviour, so they are often used to assist in simplifying electronic configurations, e.g. $1s^2$ $2s^1$ can be rewritten as [He] $2s^1$, the later noble gases are more often used in this role as writing [He] is actually no shorter than writing $1s^2$ but the point is that this truncation of the electronic configuration should be recognised as a shorthand notation commonly used by chemists. Subsequently to lithium, beryllium has 4 electrons, hence it will be written as $1s^2$ $2s^2$ (or [He] $2s^2$). After this the s orbital is filled and all additional electrons will need to be accommodated in higher energy orbitals and shells starting with the shell 2, p orbitals.

All 2p orbitals have the same energy, so the electrons occupy all three orbitals singly at first, before pairing up, which is energetically less favourable, hence the next three configurations are:

B ($5e^-$): $1s^2\ 2s^2\ 2p_x^1$ or [He] $2s^2\ 2p_x^1$

C ($6e^-$): $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$ or [He] $2s^2\ 2p_x^1\ 2p_y^1$

N ($7e^-$): $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$ or [He] $2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

After the single occupancy of each p orbital, the next three have to pair up in the remaining spaces, hence:

O ($5e^-$): $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$ or [He] $2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

F ($6e^-$): $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$ or [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

N ($7e^-$): $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$ or [He] $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2$

It is evident that the nomenclature for elements with a significant number of electrons, can be simplified using the noble gas notation but these is an additional tool of simplification that can be employed, which is to lump all of the p orbital electrons together into one term hence the three configurations above would become:

O ($5e^-$): $1s^2\ 2s^2\ 2p^4$ or [He] $2s^2\ 2p^4$

F ($6e^-$): $1s^2\ 2s^2\ 2p^5$ or [He] $2s^2\ 2p^5$

N ($7e^-$): $1s^2\ 2s^2\ 2p^6$ or [He] $2s^2\ 2p^6$

This is generally how you will see the configuration written for electrons in non-bonding orbitals, as often the outermost, bonding, electrons will be written in full with respect to their orbital occupation.

The second shell only has s and p orbitals, hence neon completes the filling of the second shell and additional electrons need to be accommodated in higher energy shells, starting with shell 3, and their orbitals in the third period. Shell three has s, p and d orbitals, but the order in which they are filled becomes more complex after 3p and the order in which orbitals fill is dealt with in the section on periodicity. After this point, the pattern of filling becomes repetitious to some extent but take care to fill the lower every orbitals first and to fill them completely.

The 3s and 3p orbitals are completely filled for argon, again a noble gas, so its electronic configuration is:

Ar ($8e^-$): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^2$ or [Ne] $3s^2\ 3p^6$

It may be expected to start filling the 3d orbitals next but these are actually of higher energy than the 4s orbital, hence, it fills first followed by the 3d level, hence, the following elements have the assigned electronic configurations:

K ($19e^-$):	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$	or	[Ne] $3s^2\ 3p^6\ 4s^1$
Ca ($20e^-$):	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$	or	[Ne] $3s^2\ 3p^6\ 4s^2$
Sc ($21e^-$):	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$	or	[Ne] $3s^2\ 3p^6\ 3d^1\ 4s^2$
Mn ($25e^-$):	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$	or	[Ne] $3s^2\ 3p^6\ 3d^5\ 4s^2$
Zn ($30e^-$):	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2$	or	[Ne] $3s^2\ 3p^6\ 3d^{10}\ 4s^2$

In contrast to the p orbitals, d level orbital fillings are almost always given as the total number of electrons in all d orbitals in that level, e.g. d^4 or d^9. From the scheme above it can be seen that zinc completes the filling of the third level of orbitals, two elements after what would be expected from the filling order used previously. It is, therefore, imperative that care is taken over writing electronic configurations, as the chemistry of zinc is affected by having complete electron shells. For those with a keener interest in the chemistry of the d-block, there is an interesting exception to the neat filling described above, which is chromium. Cr should, from the filling order described above, have an electronic configuration of $1s^22s^22p^63s^23p^63d^44s^2$ but the 6 electron in the 3d and 4s orbitals rearrange so that each orbital is occupied by a single electron, so that it is correct to write: $1s^22s^22p^63s^23p^63d^54s^1$.

Periodicity and electronic structure

Elements exhibit certain chemical properties as a result of their electronic configuration, which dictates bonding, hence, the valence (outer) shell electrons are of particular importance. The valence shell orbital type determines the block to which an element belongs. For example, en element with valence electrons in d-orbitals will be part of the d-block; this categorising suggests typical chemistry of these elements. The period itself is determined by the total number of electron shells an atom has, which are filled in an order determined by the Aufbau rule, where lower energy orbitals fill first. The order, for s, p, d and f orbital filling is generally:

1s			
2s			2p
3s			3p
4s		3d	4p
5s		4d	5p
6s	4f	5d	6p
7s	5f	6d	7p

This gives the periodic table its structure, and defines the number of other shell electrons that an element will have, in accordance with its position in a period. For example sodium (Na with 11 electrons arranged $1s^2$, $2s^2$, $2p^6$, $3s^1$) is first in its period and will have one electron in its outer shell (shell 3), while silicon (Si, 14 electrons: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$) is fourth in the same period and thus has four outer shell electrons (again shell 3, with 2 in s and 2 in p). Below this period potassium (K, 19 electrons: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$) and germanium (Ge, 32 electrons: $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^2$) will have the same outer electron numbers as the elements directly above them (this time in shell 4), and this is where ***group number*** can be useful, as it gives an idea of the outer shell electron number. The fact that there are 10 elements in-between is of no consequence, as these elements have electrons in d-orbitals of a shell below the outer one (in this case in shell 3), which fill by the time Gallium (Ga) is reached, hence, back to the same relationship as for previous periods. Note that when writing out electronic structures, it is possible to use shorthand notation of the noble gas configuration, so, for example potassium (K), which has already been given as $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, may also be represented as Ar, 4s1. This is because argon (Ar) has the electronic structure $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$ so, as this is replicated in potassium's structure the shorthand is to represent all these terms by simply writing Ar.

Oxidation state

This indicates the degree of oxidation of a given atom within a molecule, and the formal number attributed would be the theoretical charge if all its bonds to other atoms were ionic bonds. It essentially tells chemists how many electrons can be attributed to each atom in a molecule, if all electrons are assigned via a set of agreed rules. The values given are normally positive or negative integers between -4 and +8, but are occasionally zero (as for pure elements) or fractional. If an atom undergoes reaction and the oxidation number is increased, this is known as oxidation, conversely a decrease in oxidation number is referred to as reduction of that atom. The change in oxidation number is usually due to net transfer of electrons, either a gain or loss per atom. There is a common mnemonic to remember which way this occurs: **o**xidation **i**s **l**oss (of electrons), **r**eduction **i**s **g**ain (of electrons), hence **oilrig.** It should be noted, however, that oxidation and reduction refer to a change in oxidation state and transfer of electrons may not actually occur. Hence, it is more correct to define oxidation as an increase in oxidation state, and reduction as a decrease in oxidation state. Generally, these changes are caused by a transfer of electrons, thus, the accepted definition above.

Oxidation state rules

The rules used to assign oxidation sate are:

1. All pure elements have an oxidation sate of 0.
2. Simple, monatomic, ions, have an oxidation state equal to the net ion charge.
3. The charge of a polyatomic molecule or ion is equal to the sum of the oxidation states of all the constituent atoms. This allows unknown values to be determined if the oxidation states of all other species are known.
4. Hydrogen has oxidation state +1; oxygen has oxidation state -2 in most compounds. Exceptions include some metal hydrides, where hydrogen has oxidation state -1 due to the electropositivity of the metal, and peroxides, where oxygen has oxidation state -1.
5. As fluorine is the most electronegative element, its oxidation state does not change from -1; for the other halogens, they also have oxidation state -1, except when bonded to O, N or another halogen with greater electronegativity.
6. Alkali metals generally have oxidation state +1, while alkaline earth metals generally have oxidation state +2.

It is important to note that the formal charge on an atom and its oxidation state in a molecule, may not be equal; for example in ammonia (NH_3), the formal charge on the nitrogen atom is zero, whereas the oxidation state is -3. It may sometimes help to draw a Lewis structure, where the bonded structure is represented diagrammatically and valence electrons are shown with bonding electrons assigned to the more electronegative element for all atoms, to help with assigning oxidation states. This can be very useful if there are inequivalent atoms of the same element in one molecule, such as the two sulphur atoms in $S_2O_3^{2-}$, where one sulphur is bonded to the second and three oxygen atoms, this sulphur atom has oxidation state +5 whereas the terminal sulphur has an oxidation state of -1.

Transition metals

The transition metals are elements with incomplete d sub-shells, or that form cations with incomplete d sub-shells, generally with electronic structures of the form [ ]$ns^2(n-1)d^m$, where m represents the number of d-shell electrons. These metals often form coloured compounds as a result of d-d electronic transitions; they can form compounds in a number of oxidation states and/or paramagnetic compounds.

Redox reactions

In redox reactions, one species is oxidised while another is reduced by the net transfer of electron from one to the other. Redox is shorthand for reduction-oxidation. As may be expected the change in the oxidation states of the oxidised species must be balanced by any changes in the reduced species. For example the reduction of PbS to PbO by oxygen:

$$PbS + {}^{3}/_{2}O_2 \rightarrow PbO + SO_2$$

sees the sulphur lose $6e^-$, and changing oxidation state from -2 to +4, while each of the three oxygen atoms gain $2e^-$, going from 0 for the elemental form to -2. So the altered species balance each other out, it should be noted that Pb does not alter oxidation state (+2).

Within redox reactions, the pair of reactions must always occur, i.e. a reduction reaction must be accompanied by an oxidation process, as electrons are transferred from one species to another. Each of the singular reactions in this pair is called a half-reaction, in which the electrons lost or gained are included explicitly, allowing electron balance to be accounted as well. The two sides of the reaction, given by the half reactions, should be balanced accordingly. The additional terminology comes from the definition that within redox processes, a reductant transfers electrons to an oxidant, hence, the reductant (reducing agent) loses electrons, so is oxidized, while the oxidant (oxidizing agent) gains electrons, so is reduced. The reductant and oxidant form a redox pair; this should not be confused with the term redox couple, used in electrochemistry, which describes a reducing species and associated oxidised species, e.g. Ag^+/Ag.

Each half reaction produces a standard electrode potential (E^0) as the cathode in a reaction, relative to is a standard hydrogen anode where hydrogen is oxidized: $½\ H_2 \rightarrow H^+ + e^-$, under STP. The reducing potential of each species is then given relative to this reference.

Redox reactions are industrially important in smelting, where ores are reduced to produce metals, electroplating and the manufacture of cleaning products.

Isotopes

Isotopes, a term created by Margaret Todd in 1913 to describe the species observed at the same position on the periodic table, are atoms of the same element that have different numbers of neutrons but the same number of protons.

Isotope nomenclature

The nomenclature for isotopes is to either i) write the full name of the element followed by a hyphen then the mass number of the isotope, for example carbon-12 or carbon-14; or ii) write the chemical symbol for the element, in this case C for carbon, with the atomic number of the element as a prefixed subscript and the total number of nucleons in the nucleus as a prefixed superscript, e.g. ${}^{12}_{6}\mathrm{C}$ or ${}^{14}_{6}\mathrm{C}$. As the atomic number denotes the element, which is also represented by the chemical symbol, it is somewhat redundant to include and the simplified form is used with nucleon number only, e.g. 12C or 14C.

Occurrence of isotopes

As mentioned in the previous topic, the number of protons in a nucleus indicates the element being studied and the number of neutrons gives the isotope of that element. To illustrate this, consider the case of carbon-12 (12C) and the less common isotope carbon-14 (14C) used for radiocarbon dating. 14C has a mass number (protons + neutrons) of 14, while 12C had a mass number of 12. As they contain the same number of protons, given by the atomic number for carbon, which is 6, this means 14C contains 8 neutrons while 12C contains 6. Some combinations of these values create stable molecules but each element has at least one isotope with an unstable nucleus that will undergo radioactive decay to achieve stability. Such decay can result in the loss of protons or neutrons, changing the isotope or even the element itself.

Generally, there are only a few stable isotopes for each element, most commonly 3-4; the element with the most stable isotopes is tin, with ten, and there are 26 elements that have only a single stable isotope. Once the atomic number increases to 83 and above, there are no stable isotopes for any of these species. Isotope stability is related to the ratio of protons and neutrons, and the presence of key numbers of nucleons that indicate fully occupied quantum shells can have an influence. This contributes to the inherent stability of tin as it has 50 protons, representing a filled shell. It is unusual for stable nuclei to include odd numbers of protons and odd numbers of neutrons, and only four examples do: ${}^{2}\mathrm{H}$, ${}^{6}\mathrm{Li}$, ${}^{10}\mathrm{B}$ and ${}^{14}\mathrm{N}$, this is due to the fact that such odd-odd nuclei easily undergo beta decay to the more stable even-even product, which is more strongly bonded as a result of the effect of nuclear pairing. Such unstable isotopes are also called radioisotopes due to their radioactive decay behaviour; they may also be referred to as radionuclides (see below). The total number of stable and radioactive isotopes, including those created under laboratory conditions, is in excess of three thousand separate species.

Another term that is often used is nuclide; this is an atom with a nucleus composed of a set number of protons and neutrons, for example ^{14}C contains 8 neutrons and 6 protons. Grouping species together by nuclear number, called the nuclide concept, places importance on nuclear properties rather than chemical properties (the isotope concept). It is important to understand the difference between these terms, although they will often be used, erroneously, in place of each other.

Chemical and physical properties

As mentioned above, grouping atoms by the isotope concept collects atoms together in terms of chemical character. This is due to the fact that different isotopes of the same element have the same number of protons (atomic number) and electrons, giving them similar electronic structure. An exception to this is the observation of kinetic isotope effects where the differences in mass between some isotopes of the same element cause variations in the behaviour, such as the slowed rate of reaction for heavier species. There is a marked effect for hydrogen and deuterium as the additional neutron mass makes a relatively larger difference to the mass than for heavier elements, where one more neutron would be a small percentage increase.

Atomic masses of isotopes

The atomic mass of an element, as can be seen from the periodic table, are not always integers, and this is a consequence of isotopic distribution. The mass is an average over the natural abundance of all the different naturally occurring isotopes in the ratio that that are present. The average relative atomic mass (*RAM*) for an element with *n* naturally occurring isotopes, may be calculated using:

$$\mathrm{RAM} = \sum_{i=1}^{i=\mathrm{n}} m_i a_i$$

where m_i and a_i, are the atomic mass and natural abundance, in relation to the whole distribution, of isotope i, respectively.

Applications

Isotopes are useful in several applications but the separation of individual isotopes for use is still a major technical issue, especially for the heavier elements including uranium. For some lighter elements, gas diffusion of key compounds can be employed using a physical difference, however, for hydrogen and deuterium, chemical separation methods can be used. Heavier elements can be separated into their isotopes again by gas diffusion but other separation techniques include gas centrifugation and laser ionisation. Analysis of the relative abundances of certain elements in a given sample can be used to detect contamination of food and drink samples, as well as identifying meteorites or soil samples.

Providing a pure isotopic sample is available, such species can be used in chemical reactions as tracers or markers, which can be monitored using infrared spectroscopy or mass spectrometry; radiative detection methods can be employed but only if radioactive isotopes have been employed. Radiometric labelling, as it is called, is useful in radiocarbon dating where the relative amount of carbon-14 and the known half-life of that isotope are used to determine the date of formation of an artefact. There is significant use of radioactive isotopes in the nuclear power industry and in the production of nuclear weapons. The use of labels in chemical reactions can also be used to determine the mechanism of reaction through the kinetic isotope effect.

It is not only the difference in masses of isotopes that makes them useful;the fact that some exist with zero nuclear spin makes them invaluable in applications such as nuclear magnetic resonance (NMR) spectroscopy. These are usually the less common isotopes of the elements listed in the periodic table and nitrogen-15 is an example. The fact that some isotopes undergo specific nuclear transitions is exploited in Mőssbauer spectroscopy, which can be used for example to monitor catalyst phase transformations in Fischer-Tropsch synthesis, used to manufacture hydrocarbons.

Kinetic isotope effect

This is most often the difference in reaction rate as a ratio of two different isotopes within a chemical reaction or process. Altering an isotope within a chemical system, very often replacing deuterium for hydrogen, can dramatically affect the reaction rate. If the substituted isotope is involved in the rate determining step this is called a primary effect, and secondary effects are observed when the substituted group is not part of a bond either broken or formed in the reaction.

The differences in reaction rate upon isotopic substitution is attributed to the difference in vibrational frequency of the chemical bond broken or formed. As the vibrational frequencies of chemical bonds are affected by the masses of the groups at each end, then the greater the difference in mass of the two isotopes used, the greater the kinetic isotope effect observed; this accounts for the common substitution of deuterium for hydrogen as the mass is doubled. The change in vibrational frequency alters the strength of the bond, which, in turn, alters the activation energy required for bond cleavage, hence the rate of breakage. For deuterium, this would increase the mass of the isotope, decreasing the vibrational energy of the bond, increasing the activation energy and reducing the rate. Sometimes, the rate of reaction upon deuteration is seen to increase and such cases are known to exhibit an inverse kinetic isotope effect.

Radioactive decay

Isotope atoms can often have unstable nuclei, which will try to become stable by the spontaneous emission of ionising particles. The process is monatomic, i.e. no other species are required to interact with the decaying atom, with the process usually confined to the nucleus of the atom but that may require the capture and internal conversion of one of the atoms inner electrons. Once radioactive decay has occurred, it does not mean that the nuclide formed, known as a radiogenic nuclide, is stable itself and further decay may occur, by a sequence known as chain decay. Within the process the initial nuclide is called the ***parent*** and the nuclide formed by decay is known as the ***daughter***, due to the nature of radioactive decay, the parent and daughter may not be the same element, a process known as ***nuclear transmutation***. Although radioactive decay is random on a single atom scale, with the exact moment of decay being unknown, a sufficiently large sample of the same nuclide will have a calculable decay profile over any given time.

There are a number of different decay mechanisms, which can affect either or both the mass or atomic number, by either increasing or decreasing the value. For example in alpha decay, an alpha particle is emitted from the nucleus, reducing the mass number by 4 and decreasing the atomic number by 2. Within the decaying system, all mass is conserved, however, as radiation is involved, there is a need to re-establish an equilibrium within the system before each particle will achieve its rest mass.

Measuring activity

The radiation emitted by decaying particles is measured using either the S.I. preferred Becquerel (Bq), defined as one decay per second, or the Curie (Ci), which is the related to the decay of a specific isotope (radium-226) and is equal to 37 GBq. Species with particularly low decay rates may be recorded in decays per minute (dcm).

Half-lives – the time taken for half of the radionuclide atoms in a given sample to decay is known as the half-life, designated $t_{½}$, and can be found from the exponential relationship with decay constant (λ) using:

$$t_{½} = \frac{\ln 2}{\lambda} = \tau \ln 2$$

The second relationship can be made as the mean lifetime, the average lifetime of a single radionuclide, $\tau = 1/\lambda$. Hence, it can be seen that a nuclide with a large decay constant has a short half-life. Typical decay constants vary from 10^{-23} to 10^{26} seconds, showing a large variation in nuclide stability.

Activity – as stated before, the decay of single species is stochastic but the decay of a population of N particles will be predictable over a partciular time interval (dt), so the ***total activity***, i.e. the number of decays the population will undergo in dt is given by:

$$A = -\frac{dN}{dt} = \lambda N$$

Solving the first-order differential equation above gives:

$$N(t) = N_0 e^{-\lambda t} = N_0 e^{-t/\tau}$$

N_0 is the initial number of radionuclides that may undergo decay, i.e. the zero time value. Again the second relationship results from the fact that $\tau = 1/\lambda$.

The equation for total activity may also be amended to allow evaluation of the rate of decay per second per mass or volume of isotope, known as the ***specific activity***, S_A:

$$S_A a_0 = -\left.\frac{dN}{dt}\right|_{t=0} = \lambda N_0$$

With a_0 representing the amount of active material present at the start of the decay process.

Molecular structure

Molecular structure of simple molecules can be crucial in understanding the reactivity of the compound and the potential products from a given reaction. Electronic structure has been discussed previously and here consideration is given to the modes and orientation of bonds, which will give rise to the shape of each molecule.

Valence shell electron pair repulsion (VSEPR) theory

VSEPR theory uses the electrostatic repulsion between electron pairs to predict the shape of molecules, as the valence electron pairs that surround each atom in a molecule will mutually repel each other, forcing the bonds to orient into an arrangement that minimises the repulsive forces of all bonds. The steric number of an atom can help in assessing the shape as it indicates the number of electrons pairs for that atom, irrespective of whether the pairs are bonding or non-bonding.

Comparison to other models

In contrast to the bonding models discussed in the Atoms and Bonding chapter, which consider bonding orbitals for molecular shape, with the formation of sigma and pi bonds, as in valance bond theory and molecular orbital theory, VSEPR is considered rudimentary; although VSEPR often gives accurate predictions of molecular geometries for covalently bonded molecules.

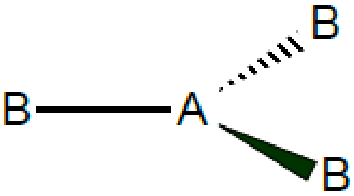
Determining molecular structures

As there are many atoms in even the most simple molecules, the theory focuses on considering the bonds formed by one or two central atoms, which are themselves bonded to two or more atoms; the geometries conferred to these selected atoms provides the shape of the overall molecule. Lewis structures have been discussed earlier, and these can be used to determine the number of electron pairs in the valence shell of a selected atom; this can be extended to show electron lone pairs and projecting bonds. Double and triple bonds are treated as though they contain only one electron pair. Where a molecule has two or more resonance forms, VSEPR can be applied to any of the structures.

As each atom is considered to be a sphere, the bonds coming from the atom can orient themselves anywhere over the surface, producing a full three dimensional geometry for that atom. An easy example to begin with is carbon dioxide, which has two oxygen atoms bonded to one carbon atom, via two separate bonds; each C=O bond experiences the lowest repulsion from the other when they are diametrically positioned, and the molecule is linear, as below:

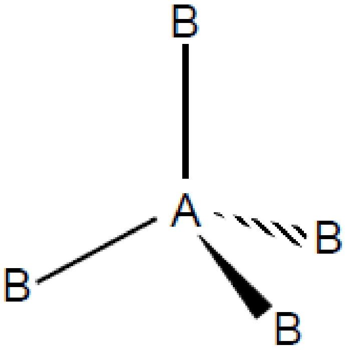
linear molecular geometry

Extension to three electron pairs, sees the atoms bonded to the central atom, adopt the vertices of an equilateral triangle around the selected atom, as in a trigonal geometry.



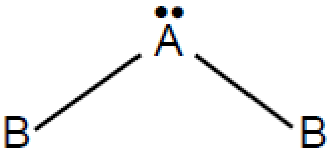
trigonal pyramidal geometry

Four electron pairs moves the arrangement from two dimensions and the geometry becomes tetrahedral, with each of the connecting atoms adopting the vertices of a trigonal pyramid (an equilateral triangle, with all three points meeting at a fourth point in the space above) around the selected atom.



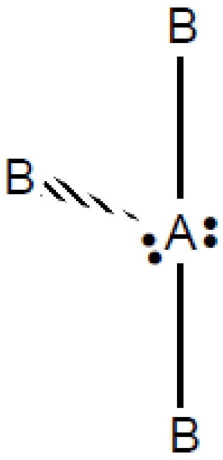
tetrahedral geometry

The geometry can be affected by whether the electron pair is shared with another atom in a bond, or if it is a lone pair, which will be held more strongly to the central atom. The lone pairs, therefore, exert a greater repulsive force than bonding pairs, reducing the angle between bonding pairs:



trigonal pyramidal geometry with one lone pair of electrons on A

Lone pairs will most strongly repel other lone pairs, while bonding pair-bonding pair repulsions are weakest, with mixed repulsions somewhere in-between, hence, the lone pairs repelled by other lone pairs will tend to occupy the sites of least repulsive force. An example of the importance of inequivalent sites in structure is the five electron pair arrangement of trigonal bipyramidal (imagine two trigonal pyramids glued together on one face). Here, the three sites in the same plane have the same repulsion, which is less than that felt by the two sites out of the plane.



trigonal bipyramidal geometry with two lone pairs of electrons on A

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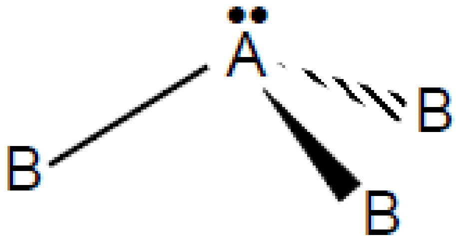
The existence of lone pairs, occupying given sites in a molecular geometry, can also explain the differences in shapes of molecules with equal numbers of atoms, for example CO_2 is linear, as all the electrons are involved in two bonding pairs, however, SO_2 is 'bent', as there are two bonding pairs and one lone pair on the central sulphur atom; the three bonds adopt a trigonal arrangement, but there are only connecting atoms on two bonds, ideally the bonds should be 120° apart but the lone pair repulsion to the bonding pairs will cause a contraction in the angle between the two oxygen atom bonds. It also explains the structure of ammonia, NH3, which should be trigonal, but the lone pair of electrons from the nitrogen forces the geometry to be tetrahedral with the lone pair making the fourth point.



tetrahedral geometry with one lone pair of electrons on A

For water, there are four pairs, hence the structure should be trigonal pyramidal, however, there are two lone pairs and two bonding pairs, hence the geometry adopted will again be bent and the bond will be smaller than the 109.5° expected for the trigonal pyramid, at only 104.5°, as the lone pairs exert greater repulsion on the bonding pairs. Hence, the description of a 'bent' molecule is based purely on the orientation of the atoms in the molecule, not the overall electronic arrangement within the molecule.

tetrahedral geometry with two lone pairs of electrons on A

Predicting molecular geometries

The steric number of an atom, A, in conjunction with information on the number of bonding (B) and lone (L) pairs in a molecule allow the structure to be predicted, and the table below shows the geometries expected for the simple steric arrangements most often encountered.

Molecular description	Shape	Example
AB_1L_x	diatomic	N_2
AB_2	linear	CO_2
AB_2L_1	bent	SO_2
AB_2L_2	bent	H_2O
AB_2L_3	linear	XeF_2
AB_3	trigonal planar	SO_3
AB_3L_1	trigonal pyramidal	NH_3
AB_4L_0	tetrahedral	CH_4
AB_5L_0	trigonal bipyramidal	PCl_5
AB_6L_0	octahedral	SF_6

Note that it is possible for A to equal B.

When different substituents (B) are present in the molecule, the predicted geometry is generally still observed, but there may be some change in the bond angle therein.

Exceptions to VSEPR

As with most rules, there are exceptions to VSEPR, where the model fails to predict the geometry correctly; one such category of molecules is transition metal compounds. The main reasons for this failure are the fact that there are no valence shell lone pairs and d-shell electrons will interact with ligands within the system. The geometries of such compounds can often be predicted by either VALBOND theory, which is based on valence bond theory and considers sd hybrid orbitals and the three centre/four electron bonding model, or crystal field theory, which takes the degeneracies of electronic orbital (usually d or f) states, caused by an inherent charge distribution from neighbouring atoms, into consideration.

Mass and volume

Chemical engineers have to design individual process units, i.e. reactors, distillation columns, heat exchangers, supervise the operation of a process or modify the design to accommodate changes in feed. So within process systems, chemical engineers monitor and control the flow of mass and energy within each unit. Considering mass in this case, it is most commonly controlled through mass, molar or volumetric flowrates and a key skill is to be able to work within all three sets of units and convert easily betweem them. Chemical engineers must be comfortable quantifying compositions, amounts and conditions of materials that enter and leave a process unit, requiring definitions that are recognised as the technical chemical engineering language.

Mass

The language associated with mass is a significant issue, hence, it is important to understand the nomenclature used and appreciate its usage. The resistance of an object to its change in velocity is a quantitative definition of mass, and it is commonly accepted that inertial mass, which determines an objects acceleration in the presence of any applied force (recall a = F/m), active gravitational mass and passive gravitational mass are all equal quantities. It is, however, essential to differentiate between mass and matter, as all matter has mass but mass is not solely attributable to types of matter, as many types of energy also exhibit mass, for example kinetic or potential energy, and photons in electromagnetic radiation.

Many people use mass and weight as the same term and weight is often quoted in mass terms, e.g. kilograms, when this should really be Newtons as weight is mass multiplied by gravitational force. This is an incorrect interchange and should be avoided in scientific working, due to the fact that, at zero gravitational force, weight can be zero but mass can never be zero.

Within a given system, mass conservation must be obeyed over any time period as mass cannot be created nor destroyed. As it has been mentioned that some energies have a mass associated with them, it is sometimes necessary to incorporate an energy term into a mass balance to make it valid.

Volume

The amount of three dimensional space enclosed by a closed system, for example the space occupied by a gas in a container, is known as the volume of the system. The units most commonly used for volume are the derived units of litre (L) or cubic metre, from length cubed. The unknown volume of a given solid, of any shape, can be found by fluid displacement, this method can also be used to determine the volume of some gases but caution is required as gases often dissolve in the fluid and the total volume of the combined system is not additive.

Mass and Volume

Mass and volume are related by ***density***, which is defined as mass per unit volume with units including kg/m^3, lb/ft^3 etc. Density is a useful quantity as it is independent of temperature for solids and liquids. Chemical engineers also use the term ***specific volume***, which is volume per unit mass and measured in m^3/kg, ft^3/lb etc. It should be evident that specific volume is the inverse of density.

The density of a substance can be used as a conversion factor to relate the mass and volume of a quantity of substance via:

$$\text{mass} = \text{volume} \times \rho$$

where ρ (rho) is the symbol for density.

Mass and Volumetric Flowrate

In continuous chemical processes material will move from one point to another, sometimes between process units; hence a static mass or volume measurement is of little use. The rate at which material is transported is called a flowrate and can be expressed as mass flowrate (mass per unit time, e.g. kg/hr) or volumetric flowrate (volume per unit time e.g. m^3/hr).

Mass and volumetric flowrates are related through density, in a similar fashion to the static system:

$$\text{mass flowrate} = \text{volumetric flowrate} \times \rho$$

In industry it is frequently easier to measure volumetric flowrate. Therefore the mass flowrate is commonly calculated from the volumetric flowrate and the density of the stream fluid.

Within calculations it is usual to use a symbol with a dot above it e.g. $\dot{m}$ to denote a flowrate of that parameter, this symbol would indicate a mass flowrate.

Mass and Mole Units

Two of the first skills required by a chemical engineer are to be able to express compositions and to be able to convert between mass and mole units. For this, consider the periodic table, met previously, this allows us to understand determine the mass of a standard amount of material, known as the mole (discussed in the next topic). By being able to determine molar quantities from masses, chemical engineers can calculate many physical parameters for a given system.

The mole

The Periodic Table was described earlier, and represents all the known elements, grouped according to chemical properties. The table displays information about all the elements including their relative atomic mass, which is a critical quantity in the concept of the mole.

The mole

Considering the reaction that would occur between elements to form molecules, it is easy to see that specific numbers of building blocks are required to react with each other to create these larger structures. So starting with the Periodic Table and atomic masses, it was decided in the 1960s, after several other models were dismissed, that the concept of a mole as a unit of measurement of the amount of a material would be based on the number of atoms that compose 12 g of isotope Carbon-12. Within this mass there are $6.02214179 \times 10^{23}$ atoms, which is referred to as Avogadro's number (N_A). Avogadro first suggested that the number of molecules in a set volume of gas, at fixed temperature and pressure, is the same regardless of the gas, hence, the constant used today is closely related to this hypothesis and bears his name. The value of $6.02214179 \times 10^{23}$ atoms is the number of atoms in one mole.

Atomic mass unit (amu) and atomic weight

A single ^{12}C atom, at rest, is assigned a mass of 12 atomic mass units (amu) so, as carbon-12 contains 6 protons and 6 neutrons in the nucleus, 1 amu is approximately the average mass of proton/neutron. Given 1 atom of ^{12}C will weigh 12 g/($6.02214179 \times 10^{23}$) = 1.9926×10^{-23} g, which is also 12 amu, hence, 1 amu has a mass of 1.6605×10^{-27} kg.

This forms the basis of all the atomic masses observed in the Periodic Table, ^{12}C has 6 protons and 6 neutrons, so has an atomic weight of 12, similarly ^{42}Ca has 20 protons and 22 neutrons, so an atomic weight of 42 (such calculations are typically correct to < 1%). The masses used for each element are normally the average mass taken as the proportions of their naturally occurring isotopes. So, for instance, chlorine has an atomic weight of ~35.45, as a result of it being about three quarter ^{35}Cl and one quarter ^{37}Cl in its natural abundance. The molecular weight of a substance is found from the sun of the atomic weights of all the individual components constituting a molecule of the compound.

The individual masses of atoms are too small to work with directly; hence, chemists use the concept of the mole and scale the mass of an element by a given number of particles (N_A) such that a mole always contains the same number of elementary species.

Units of the mole

As with the units met previously there are many ways of representing the unit of measurement of the amount of material, the most commonly use of which is the 'gram mole'. This is a mass in grams that is numerically equal to the molecular weight and is used to convert between mass and mole units. The same definition holds for other units of mole, but the mass units must also be carefully considered. These alternate units include kg-mole (kmol), lb-mol and ton-mol and each has its mass unit defined in its name. Consider the example of CO, which has a molecular weight of 28, so the molar quantities would be one g-mole (mole) of CO contains 28 g, one kg-mol (kmol) contains 28 kg and one lb-mol contains 28 lb. It is rare to see g-mole and kg-mole used in their expanded nomenclature and, most often, mole and kmol will be used.

From the example above it should be appreciated that if the molecular weight of a substance is M, then there are M kg/kmol, M g/mol and M lb/lb-mol. This is useful information as molecular weight can be used as a conversion factor between mass and mole:

$$\text{mole} = \frac{\text{mass}}{\text{molecular weight}}$$

Mass and molar conversion – as a consequence of the relationship between molar quantities, it follows that mass conversion factors are equal to molar conversion factors. So in the way that:

$$1\ \text{kg} = 1000\ \text{g} = 2.205\ \text{lb}$$

So does $$1\ \text{kmol} = 1000\ \text{mol} = 2.205\ \text{lb-mol}$$

Mass and mole fraction – often a process stream will contain more than one substance, and it is necessary to be able to determine the contributions of each species to the mixture. The following terms are used to define the composition of a mixture:

mass fraction, $x_A = \frac{\text{mass of A}}{\text{total mass}}$ and mole fraction, $y_A = \frac{\text{moles of A}}{\text{total moles}}$

When using these values or determining them, it is essential to choose a valid basis for the calculation so if data is provided in terms of mass (e.g. % mass) then a basis of 100g could be chosen; if data is provided in terms of moles (e.g. % by moles) then a basis of 100 moles would be most suitable.

Average molecular weight – this represents the average mass of one mole of a gas mixture and can be calculated using:

$$\text{average molecular weight} = \frac{\text{total mass}}{\text{total number of moles}}$$

The average molecular weight is a useful quantity in determining reaction ratios and physical properties that are mass dependent.

Stoichiometry

The mole is a useful quantity in determining the amount of material that is present in a system or that might be required in a reaction. When considering chemical reactions, the ratio of each species required to take part in the reaction can be one of the most important pieces of information. It allows a chemical engineer to determine how much material is required or, more importantly, the minimum amount of a cheaper reagent that they can supply to maximise the conversion of a more expensive substance. The ratios required for each element or molecule are known as the stoichiometry of the reaction.

Stoichiometry

Stoichiometry is the theory of the proportions in which chemical species combine with one another. The use of the concept of the mole is vital when dealing with chemical reactions. For example, consider the following reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The chemical equation is balanced, i.e. there is the same number of each atom type of the left and right hand sides of the reaction. The balanced equation shows the relative number of moles (or molecules) of reactants and products involved in the chemical reaction, indicating the stoichiometry of the reaction. The numbers written before the species in the chemical reaction are called the ***stoichiometric coefficients***.

When performing stoichiometric calculations, remember that these are only valid on a molar basis, so convert all mass quantities provided to moles, this allows the others quantities to be determined by the use of ratios and multiples. It is always possible to convert the number of moles back to a mass at the end, if this is desired. When working with molar quantities ensure that any molar units are consistent throughout the calculation e.g. lb-mol, kmol, mol, any can be used but must be maintained in working. In such calculations, total mass must be conserved, i.e. the total masses in and out of the system must tally, and it must be borne in mind that a balanced reaction is no proof of a feasible reaction, which must be determined thermodynamically. Similarly, there is no information regarding the rate at which the reaction will proceed, the degree of completion that will be achieved or the possibility of unwanted side reactions.

Molar flowrate

In many processes, there will not be a static system but a flowing process stream, so the molecular weight is used to relate the mass flowrate of a continuous stream to the molar flowrate:

$$\text{molar flowrate, } n_f = \frac{\text{mass flowrate}}{\text{molecular weight}}$$

It should be clear that this now provides an easy route to convert volumetric flowrates into molar quantities, but using the methods outlived in mass and volume.

Industrial considerations

Exact stoichiometric amounts are rarely used in industrial processes and companies often increase the conversion of an expensive reactant, by adding other reactants in excessive quantities. This means that the product streams will also commonly contain these excess reactants. Such methods can be used to prevent unexpected side-reactions that can also occur, limiting conversion to the desired product. The conversion can also be increased by recycling key feeds, this can affect the equilibrium of a system and drive the reaction toward further production of desirable products.

Acid-base chemistry

Definition of acids and bases

The chemical interaction between an acid and a base is known as an ***acid-base reaction***, which varies depending on the species involved. Historically, the theory of acid-base chemistry was thought to be related to the composition of the compound, specifically that it should contain oxygen; this was the theory of Antoine Lavoisier but was disproved some years later by Sir Humphry Davy when he proved non-oxygen containing species, such as hydrogen sulphide and the hydrohalic acids, existed. This work was extended by Liebig, who proposed that acids are substances that contain hydrogen that can be displaced by a metal species before being formulated into the currently accepted ***Arrhenius definition*** of a acid as a substance that dissociates in water to produce hydrogen cations (H^+), while a base dissociates in water to form hydroxide anions (OH^-). It should be appreciated that H^+ ions do not exist as separate species in a solution but rather that the hydronium cation (H_3O^+) is actually formed.

This forms the basis of the statement that the reaction of an acid and a base will produce a salt and water in a neutralisation reaction, as the hydrogen cations form a compound (water) with the anion from the base (i.e. hydroxide anion) and the cation from the base, often a metal, will react with the anion from the acid to form a salt. For example the reaction of potassium hydroxide and nitric acid:

$$H_2NO_3 + 2KOH \rightarrow K_2NO_3 + 2H_2O$$
$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

Note that the Arrhenius definition only holds for aqueous systems and that the dissolution of acids in other solvents would not necessarily be acidic, similarly molten metal hydroxides are not basic. The issue of the solvent used was resolved with the generalisation offered by the ***solvent system theory***, devised by Albert Germann. He noted that in several solvents, there is a presence of solvonium cations and solvate anions in equilibrium (see chapter on equilibria for more information) with undissociated solvent molecules. The simplest example is water itself, which exists as water with some hydronium cations and hydroxide anions. The addition of another substance, i.e. a solute, to the solvent causes a shift in this equilibrium to form either more solvonium cations or solvate anions, depending on its nature. An acid increases the solvonium cations present, while a base increases the concentration of solvent anions. For example, water exists as:

$$2xH_2O \leftrightarrow xH_3O^+ + xOH^-$$

Addition of the acid H_2NO_3 will form more hydronium cations:

$$2xH_2O + yH_2NO_3 \leftrightarrow (x+2y)H_3O^+ + yNO_3^- + xOH^- \qquad (x \rightarrow 0)$$

While the presence of the base KOH will increase the presence of hydroxide anions:

$$2xH_2O + zKOH \leftrightarrow xH_3O^+ + zK^+ + (x+z)OH^- \qquad (x \rightarrow 0)$$

The strength of this approach, in terms of solvent rather than only water, is demonstrated by consideration of aprotic solvents, such as liquid N_2O_4:

$$AgNO_3 + NOCl \longrightarrow AgCl + N_2O_4$$

$$\text{base} + \text{acid} \longrightarrow \text{salt} + \text{solvent}$$

As a result of the interaction between the basic/acidic species and the solvent, the nature of a substance can be altered by changing the solvent for example perchloric acid, which is a strong acid in water, is a weak acid in ethanoic acid yet a weak base in fluorosulphonic acid. This approach has been criticised but it is important to appreciate the changing nature of compounds with regard to their environment, which can have consequences for reaction and materials choice.

Brønsted-Lowry acids and bases

Working independently, Johannes Nicolaus Brønsted and Martin Lowry developed a definition, underpinned by the concept of base protonation and acid deprotonation, where acids have the ability to *donate* hydrogen cations (H^+) to bases, hence the acids *accept* these H^+ ions. This definition removes the reliance on a full system description, i.e. the solvent or salt formed, but rather focuses on the acid and base themselves. The species involved in the transfer of a proton are known as a ***conjugates*** (i.e. a pair), with a conjugate acid and conjugate base produced.

By this definition, i.e. acids donate protons and bases accept them, an acid-base reaction is, therefore, the transfer of a hydrogen cation from an acid to a base. Thus the acid and base react, not to given a salt and solvent, but rather a new (conjugate) acid, the base with accepted H^+, and new (conjugate) base, the acid with H^+ removed; consequently eliminating the idea of neutralisation.

For example, the addition of hydrogen cations (H^+) to hydroxide anions (OH^-), which are basic, produces water (H_2O); hence water is the conjugate acid of hydroxide ions:

$$H^+ + OH^- \longrightarrow H_2O$$

As mentioned above, the solvent is no longer considered, however, the solvent system can co-exist within the Brønsted-Lowry definition, which can also provide an explanation for the low concentrations of hydronium and hydroxide ions produced by the dissociation of water:

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$

where water, which is amphoteric, acts as both acid and base; as one molecule of water donates a H^+ ion, forming the conjugate base, OH^-, with a second molecule of water accepting the H^+ ion, forming the conjugate acid, H_3O^+.

In general, for acid–base reactions, the Brønsted–Lowry definition is:

$$AH + B \rightarrow BH^+ + A^-$$

where AH is the acid, B is the base, BH^+ is conjugate acid of B, and A^- is the conjugate base of AH.

Lewis acids and bases

In contrast to the Brønsted-Lowry definition of acids and bases, Lewis defined the species in terms of electron transfer rather than hydrogen cations. Hence, a ***Lewis base*** is a species that donates an electron pair to a ***Lewis acid***, which accepts the donated electron pair. This concept is most easily demonstrated by considering the established aqueous acid-base reaction:

$$HCl + NaOH \rightarrow H_2O + NaCl$$

Here the acid combines with the base, rather than exchanging atoms with it; the acid is H^+ and the base OH^-, which has an unshared electron pair that it is able to donate, Hence, the acid- base reaction is not the transfer of H^+ but the donation of an electron pair from OH^-, forming a covalent bond to produce water. The electronic interactions involved are the donation of electrons from the highest occupied molecular orbital (HOMO) of the subsequently known base to the lowest unoccupied molecular orbital (LUMO) of the second species, then known as the acid.

The strength of a Lewis acid and base interaction is determined by the concentrations of all solution species, for a simple system:

$$A + B \leftrightarrow AB$$

The stability constant is given by:

$$K = \frac{[AB]}{[A][B]}$$

where a high value of K indicates a strong interaction as [AB] is large compared to the product of [A][B]; similarly a low value of K indicates a weak interaction. The interactions is usually governed by the relative strengths of the acid and base, which can be either hard or soft.

Hard acids and bases are usually small species that are difficult to polarise, e.g. hard acids: H^+, Na^+, Al^{3+}; hard bases: OH^-, F^-, NH_3. In contrast, ***soft acids and bases*** are usually large species that are easily polarised, e.g. soft acids: Ag^+, Cd^{2+}, Cu^+; soft bases: H^-, I^-, CO. This is an important distinction as hard acids tend to bind to hard bases, as they both exhibit high ionic character so K is high, and soft acids tend to bind to soft bases, which both exhibit significant covalent character and, again, K is high. Any soft-hard interaction will have a low K as the interaction will be poor.

Reactions of acids and alkalis

This is a particular acid-base reaction, where the base is also an alkali species, meaning it is a basic, ionic salt of either an alkali or alkaline earth metal. In this instance, the reaction produces a metal salt and water in a neutralisation reaction. The acid either contains hydrogen cations or causes them to be produced in solution, while the alkali is a soluble base either containing hydroxide ions or causing them to be produced in solution. For example, nitric acid and potassium hydroxide:

$$HNO_3 \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$$

$$NaOH \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

As a result of the neutralisation of either the acid or base, by the other species, into water, such reactions have a number of applications including within antacid formulations, where excess hydrochloric acid in the stomach is neutralised, most commonly, by species including sodium carbonate and aluminium hydroxide. Neutralisation can also be used for the regulation of pH in agriculture via the application of fertilisers, or the abatement of acid formation by the removal of sulphur from fuel before combustion to avoid the formation of sulphur dioxide, and, subsequently, acid rain.

Acid-base titrations

The most commonly used laboratory method for the determination of an unknown analyte, i.e. the species of interest, is called a titration and this is very often utilized in acid-base chemistry. The technique is a quantitative, mostly, volumetric analysis. A standard solution titrant of either the acid or base is prepared, with a known concentration, and the volume of this solution required to react with a given amount of the analyte determines its concentration. An indicator is routinely used to determine the end-point of the titration where a lasting colour is either removed or produced at the end-point. Such indicators that are often encountered include methyl violet 10B (low pH: yellow; high pH: violet); bromophenol blue (low pH: yellow; high pH: purple); methyl orange (low pH: red; high pH: yellow); methyl red (low pH: red; high pH: yellow); phenolphthalein (low pH: colourless; high pH: magenta). Universal indicator can indicate pH over the whole range but is merely a mixture of several indicators that act across the spectrum.

Complexometric titrations

It is common for complexometric titrations to be used in systems involving metal salts, where the formation of a coloured complex indicates the end point of the titration, as it can differentiate between different metal ions; ethylenediaminetetraacetic acid (EDTA) is often used as a titrant, acting as a Lewis base by electron donation from the four carboxyl and two amine groups. A suitable indicator, that produces an unambiguous colour change, is used to determine the titration end-point; these are generally organic dyes, such as Eriochrome black T.

Redox titrations

Within these systems there is a redox reaction that occurs between the analyte and titrant, which are generally followed using a redox indicator (and/or a potentiometer).A commonly encountered example is the titration of iodine against a reducing agent, with a starch indicator, where the dark blue colour of the complex formed between starch and iodine diminishes as the iodine is used up by the analyte.

pH

The acidity (or basicity) of an aqueous system is measured by the pH. A pH of 7 is neutral, neither acid or base, and pure water is generally accepted to have a neutral pH at STP. pH values less than 7 are considered acidic and greater than 7 is said to be basic (or alkaline). The measure is an approximation of $-\log_{10}[H]$, where [H] represents the concentration of hydronium cations in the solution; hence a low concentration, i.e. more basic conditions, will give a high pH, similarly an acidic solution has low pH. This is only an approximate relationship as pH also takes an activity factor into consideration, which accounts for the propensity of the hydronium cations to interact with other species within the solution so more correctly pH should be written as $-\log_{10}(a_{H^+})$, where a_{H^+} is the activity of hydrogen ions in mol L^{-1}. Generally, most pH values lie between 1 and 14 but there are actually no upper or lower limits on the relationship, hence, values outside of this range may be observed.

Activity is defined as the product of a concentration and the activity coefficient, which usually takes any value between 0 and 1, hence it is less than the concentration but similarly measured in mol L^{-1}. The activity is affected by the ion type, temperature and ion charge so for a strong electrolyte, the activity tends towards the concentration in a dilute solution.

pH is determined using a pH meter, which relates potential difference to (a_{H^+}), hence pH, using the Nernst equation:

$$E = E^0 + \frac{RT}{nF}\ln\left(a_{H+}\right)$$

where E is a measured potential of the solution, measured in volts (V) which are equal to J C^{-1}, E^0 is the standard electrode potential (often using a calomel electrode, and in the standard state for which the activity is one), R is the gas constant (8.3144 J K^{-1} mol^{-1}), T is the temperature in Kelvin, F is the Faraday constant (C mol^{-1}), and n is the number of electrons transferred. By using solutions of known activity, is possible to deconvolute this from and determine the concentration independently.

pOH

Similarly to pH, pOH is often used to measure hydroxide ion (OH^-) concentration, however, pOH is not an independent measurement, but is derived from pH. Hydroxide ion concentration, in water, is related to hydrogen ion concentration through the self-ionization constant of water (K_W, which is approximately 10^{-14}) by:

$$[OH^-] = K_W / [H^+]$$

Hence $$pOH = pK_W - pH$$

As a consequence pOH ≈ 14 – pH, at room temperature but this relationship is not always valid.

Strong acids and bases

Acids and bases are often referred to in terms of strength and it is useful to understand what is meant by the terms strong and weak in this context. Strong acids and bases are those that essentially dissociate (ionize) completely in water, for example hydrochloric acid is a strong acid and sodium hydroxide is a strong base. When calculating the pH of a strong acid, the baseline concentration contribution from the ionisation of water is negligible, hence, the pH is essentially a function of the concentration. This contrasts to weak acids, where dissociation of the acid is small and the baseline contribution from water is significant, within a weak acid system, as for all equilibrium states, mass balance must be obeyed so any acid dissociated is present as the conjugate base anion, hence, the relationship

$$C_a = [HA] + [A^-]$$

holds, where [HA] is the concentration of the protonated form of the acid, and $[A^-]$ is the concentration of the conjugate base anion, and C_a is constant. It should be appreciated that for a strong acid, $[A^-]$ will be much greater than [HA], so the [HA] term can be neglected, hence:

$$C_a = [A^-]$$

Within the aqueous solution it is necessary that charge neutrality is maintained, known as the ***electroneutrality principle***, across all species combined.

Weak acids and bases

In this class of compounds, there are added complications from the additional species present as a result of only partial dissociation, using the dissociation constant for the system under study; hence, for a weak acid either pK_a or K_a (acid dissociation constant) is used. K_a is related to the concentrations of all the species involved by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

As stated above, both mass and charge balance must be obeyed, hence:

$$C_a = [HA][A^-]$$

When pH is considered to be less than 6, except in the case of extremely weak acids or infinitely dilute solutions, $[H^+]$ can be assumed to be much greater than $[OH^-]$, which allows simplification of the above relationship, by $[H^+] = [A^-]$.

Applications

Within chemical engineering, it is possible to work with a wide range of pHs in the same process, with chemicals like ammonia (pH 11) and hydrochloric acid (pH 1), both concentration dependent, exhibiting extremes of the range. However, the use of raw chemicals is not the only time this may be encountered, in food processing and pharmaceuticals manufacture high and low pHs are common, for example fruit juice (pH 2-3) or milk of magnesia (pH 10).

Water is a variable quantity and, when using it as a material or amenity, it is worth considering the altered properties depending on its origin. Distilled water, as mentioned above, is essentially neutral with pH7; however, seawater is slightly basic (pH 8) while mine runoff water can even exhibit negative pHs (up to pH -3).

Basic organic chemistry

The field of organic chemistry is vast and much work is dedicated to understanding reactions in such systems in great detail to optimize processes and develop new molecules. As a chemical engineer, it will often be necessary to scale-up the manufacture of new substances or to work with chemists to improve existing processes. To this end it is essential that chemical engineers understand the language used by chemists and have a basic understanding of the factors controlling basic organic chemistry.

Basic nomenclature

Nomenclature is the term used to define the naming procedure of a given system. Chemical nomenclature may sometimes appear unintelligible but, by following the basic rules laid out here, it should be possible to work out the molecules that are being discussed.

One of the most important underpinning pieces of information in chemical nomenclature are the root names for organic chains. The names are approved by IUPAC meaning that they are globally recognised and the main root chain given in chemical compound name relates to the longest continuous chain of carbon atoms, which contain the highest priority functional group (see later).

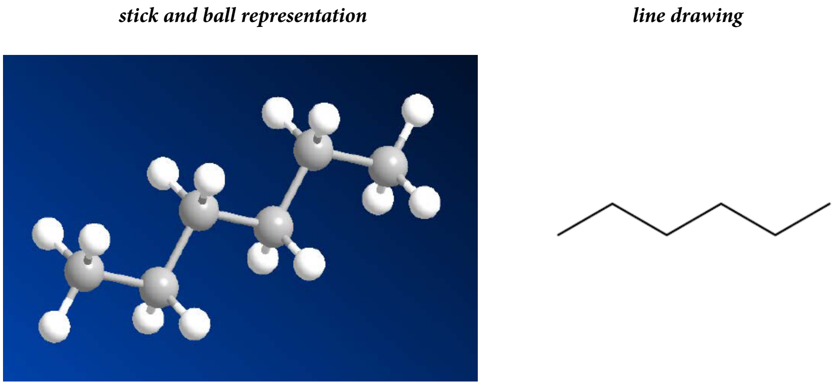
These names need to be remembered and describe chains up to and including 20 carbon atoms, but here only chains up to and including 10 carbon atoms will be discussed and this should be the most complex examples encountered.

Number of Carbon atoms in chain	Root name
1	meth-
2	eth-
3	prop-
4	but-
5	pent-
6	hex-
7	hept-
8	oct-
9	non-
10	dec-

Within organic systems, each carbon atom is able to make four bonds to other atoms, including other carbons, which should be remembered when determining structures. Several different types of simple molecules exist:

Alkanes – known as saturated hydrocarbons, these molecules only contain single bonds between the carbon atoms and no multiple bonds. The bonding consists of four sigma bonds and is known as sp^3 hybridised, as the four electrons from the four bonding orbitals are shared in one s and 3 p orbitals. The beginning of their name comes from the root name and they end in –ane (from their family name of alkane); the formula of alkanes follow the rule C_nH_{2n+2}. Hence, a chain of length 6, would be hex- plus –ane: hexane and have formula C_6H_{14}.

As a straight chain molecule, the structure would be:



stick and ball representation

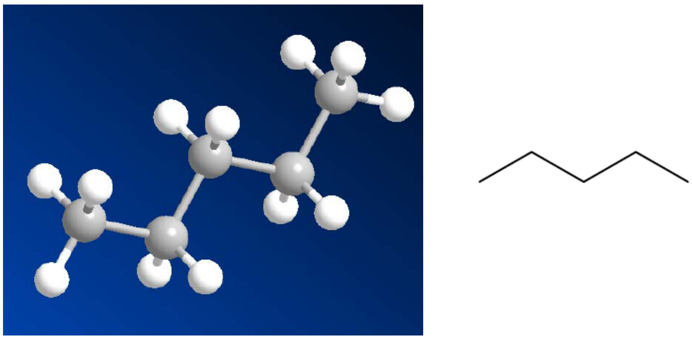
line drawing

hexane

Molecules can be depicted in a variety of ways and two of these representations are shown above. The stick and ball version shows all atoms as colour coded balls with the bonds between them represented by sticks. The line drawing simplifies the arrangement as it only shows the carbon atoms and the connectivity between them; hydrogen atoms are ignored. Similar methods can be used for any molecule but the colour of the atom will change, depending on what it is, and any element other than carbon, or hydrogen which is omitted, will be designated by the use of its elemental symbol in place of the intersect of two or more lines, as used for carbon.

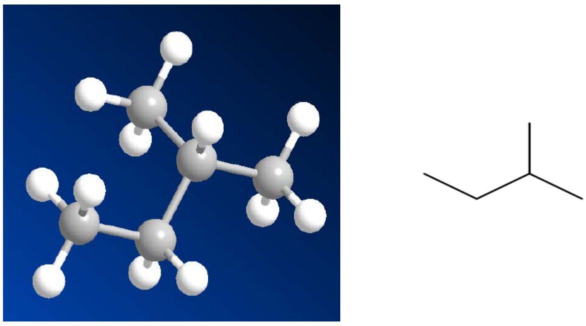
Some chemists may even represent chemical reactions, especially those involving organic reagents, as a series of line drawings, which can be used to indicate the movement of atoms within the structures that are reacting. Often, the chemist will use arrows to indicate the loss of a group or the movement of electrons within a structure. Such diagrams with notation are referred to as reaction mechanisms.

Branched alkanes – an alkane with an additional, shorter chain, coming off the longest section, is known as branched but other than that has the same bonding characteristics and generic formula as an alkane. As a result of the existence of branched molecules, several molecules can have the same formula but very different structures, these are known as isomers. An example is C_5H_{12}, which has three isomers. The first isomer is the 5 carbon chain of pentane:



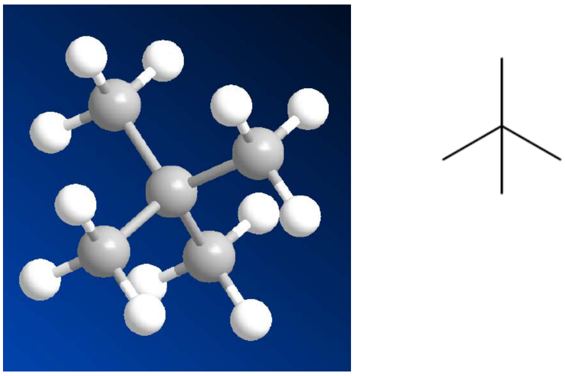
pentane

The second has the same formula (C_5H_{12}) but the carbons are bonded in a different way, giving 2-methyl-butane, as there is a four carbon chain with a methyl group attached to the second carbon:



2-methyl-butane

Lastly, the third isomer is known as 2,2-dimethyl-propane, as there is a three carbon chain with two methyl groups attached to the second carbon:



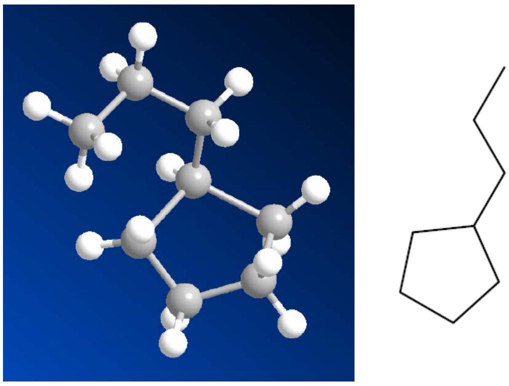
2,2-dimethyl-propane

This last isomer raises another issue in naming molecules, that of multiples of the same substituent, in this case there are two methyl groups so it is convenient to group these into one term of dimethyl. The 2,2 denotes that the two groups are both bonded to carbon 2. When grouping substituents the prefixes to use are:

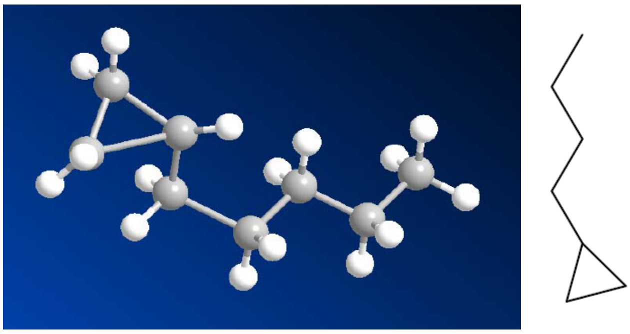
Number of substituents	Group prefix
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-
7	hepta-
8	octa-

Shorter groups are listed first, before the longer parent chain name i.e. as in the example above, 2,2-dimethyl-propane, the methyl groups are given first in the name. The groups are listed alphabetically in a molecule name rather than by carbon chain length, i.e. ethyl- would be listed before methyl-.

Cycloalkanes – these are formed by a carbon chain closing by bonding to itself at some point. An example is cyclopentane, which has five carbon atoms in a ring, the cylco- part denoting a ring is formed and pentane indicating it is an unsaturated chain of five carbon atoms. It is worth noting that the rule of listing shorter groups first is still true and care is required when substituents are longer that the parent chain forming the ring. For example compare, propyl-cyclopentane and cyclopropyl-pentane:

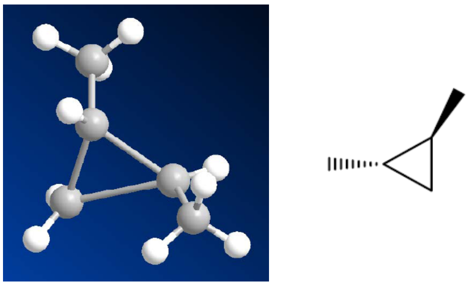


propyl-cyclopentane

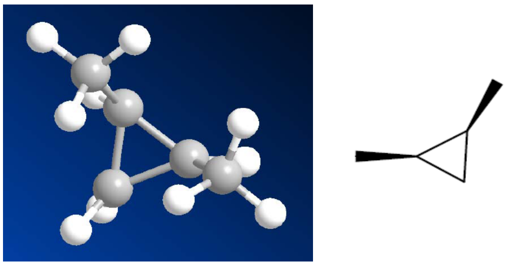


cyclopropyl-pentane

A result of the presence of the rigid and fixed structures of cyclic species is the presence of steric isomers, where the orientation of a substituent depends on specific bond direction formed during reaction. So the arrangement of the atoms is the same but their position in space is different. An example would be1,2-dimethylcyclopropane, where the two methyl groups can both be on the same side of the ring or opposite:



trans-1,2-dimethylcyclopropane



cis-1,2-dimethylcyclopropane

Hence, there are two different versions of the same molecule, with the same substituent placement, which are only differentiated by the prefixes trans- and cis-, indicating different or the same side of the ring, respectively, see the pictures above.

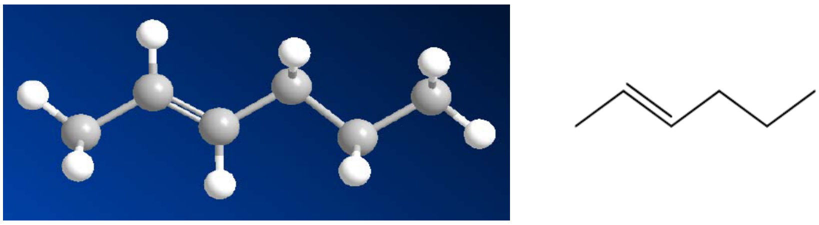
Functional groups – within organic chemistry, there are a number of additional groups of elements that need to be understood and recognised, as their presence can greatly affect a reaction pathway. This is particularly important when species that are 'good leaving groups' are present, for example the halides, as they are very electronegative, The presence of such groups can be intentional, in order to drive a reaction at a particular part of the molecule. Again, there is some related nomenclature for functional groups, which can occur in many different types of organic molecules. In the table below, there are several prefixes/suffixes that tell the reader of functional groups that are contained in a molecule. These are a small selection of a wider variety in use.

Group	Prefix/suffix	Functional group	
fluorine	fluoro-	-F	
chlorine	chloro-	-Cl	
bromine	bromo-	-Br	
iodine	iodo-	-I	
nitro	nitro-	$-NO_2$	
alcohol	hydroxy- / -ol	-OH	
ether	-ether	-O-R	
amine	amino- / -amine	$-NH_2$	(primary)
amine	amino- / -amine	-NH-R	(secondary)
amine	amino- / -amine	$-N-R_2$	(tertiary)
thiol	mercapto- / -thiol	-SH	
ketone	oxo- / -one	-CO-R	
aldehyde	oxo- / -al	-CO-H	
nitrile	cyano- / -nitrile	$R\equiv N$	
carboxylic acid	carboxy- / -oic acid	-CO-OH	
amide	carbomoyl- / -amide	$-CO-NH_2$	
acyl halides	halidealkanoyl- / -oyl halide	-CO-X	
ester	alkoxycarbonyl- / -oate	-CO-O-R	
anhydride	anhydride	-OC-O-COR	
cation	ammonio- / -ammonium	$[NR_4]^+$	
sulphide	thia- / -sulphide	R-S-R′	

In the table above R denotes a carbon chain connected to the functional group, and X is a generic halide. Alkanes are known as aliphatics, alkenes also fit into this category.

Alkenes – in contrast to alkanes, the alkene family are unsaturated species and have at least two carbon atoms within the structure that form only three bonds instead of four; at least one bond is a double bond between two carbon atoms and these three coordinate carbon atoms are referred to as sp^2 hybridised, consisting of two sigma and one pi orbitals. The beginning of their name comes from the root name and they end in –ene (from their family name of alkene); the formula of basic alkenes with only one double bond follow the rule C_nH_{2n}. Hence, a chain of length 6, would be hex- plus –ene: hexene and have formula C_6H_{12}.

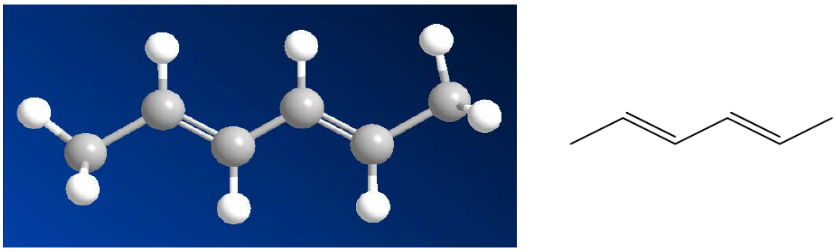
As a straight chain molecule, the structure would be:



2-hexene

It should be evident that the double bond can be present in more than one position in this molecule and its location has to be defined in the name. The example above would be known as 2-hexene, as the number is given by the first carbon of the double bond.

For ***multiple double bonds***, the formula rules are: C_nH_{2n} for one double bond (d.b.), C_nH_{2n-2} for 2 d.b., C_nH_{2n-4} for 3 d.b. and so on. The number of bonds present is also denoted in the name using the same multiple terms as for substituent group numbering, an example would be a chain of six carbons with two double bonds:

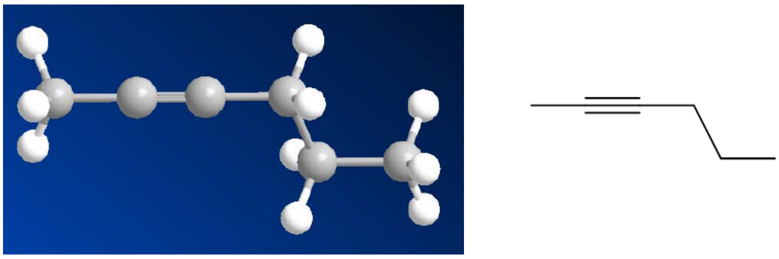


2,4-hexadiene

Note that the two double bonds occur consecutively in the molecule, such bonds are called conjugated bonds, which allow some ***delocalisation of the electrons*** in these bonds, which affects their chemistry.

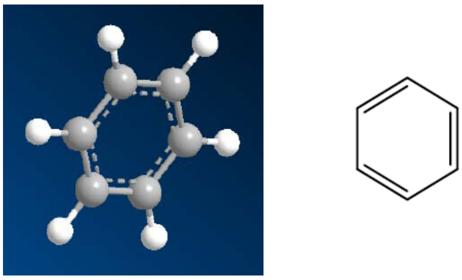
As is the case for alkanes, ***branched alkenes*** are also known and their treatment and naming is the same as for their saturated counterparts, and isomers may be formed. As the double bonds cannot rotate as single bonds can, then the formation of *cis* and *trans* isomers is also possible. These analogies are also true of cyclic alkene species.

Alkynes – are another category of unsaturated structures and have at least two carbon atoms within the structure that form only two bonds instead of the four seen in alkanes; at least one bond is a triple bond between two carbon atoms and these two coordinate carbon atoms are referred to as sp hybridised, consisting of one sigma and two pi orbitals. The beginning of their name comes from the root name and they end in –yne (from their family name of alkyne); the formula of basic alkynes with only one triple bond follow the rule C_nH_{2n-2}. Hence, a chain of length 6, would be hex- plus –yne: hexyne and have formula C_6H_{10}. The location of the triple bond must be given in the name of the alkyne.



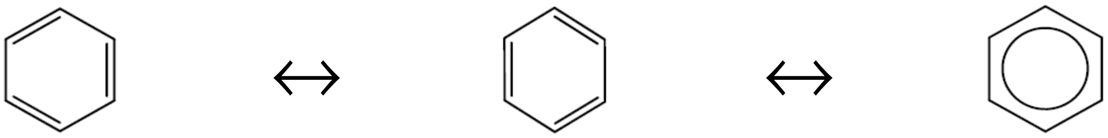
2-hexyne

Aromaticity – cyclic species were met earlier and can exist for alkanes, alkenes and alkynes, the concept of conjugation was also discussed and the existence of conjugated cyclic species leads on to aromaticity. Compounds that are aromatic, are fully conjugated cyclic (or even polycyclic) structures with a number of double bonds. Conjugation of the sp^2 hybridised occurs by the overlap of the pi orbitals of the carbon atoms and results in an inherent stability of these compounds, and reducing their relative reactivity compared with the equivalent alkene. The bonds are all planar and the electrons involved in the sp^2 bonds form a delocalised ring, containing $(4n+2)\pi$ electrons, where n is an integer, for example benzene has 18 electrons and n = 4. This is known as Huckel's rule and this relationship must be obeyed for aromatic compounds. The simplest aromatic system is benzene (C_6H_6, full name: 1,3,5-cyclohexatriene), which can be drawn as:



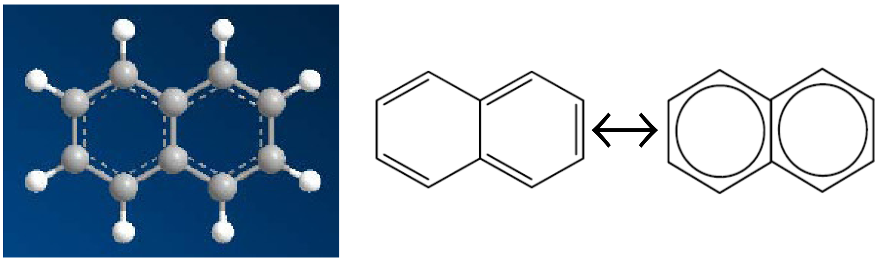
benzene

It should be noted that the line drawing has other equivalents:



The third representation indicating that the π electrons are delocalised across all carbons, hence the location of the double bonds is not fixed. The bond 'order' for benzene is $18e^-/6$ bonds = 1.5, which is a better representation of the structure than considering it as alternating single and double bonds.

Polycyclic aromatics are common and are composed of multiple benzene rings, for example naphthalene, which is the primary ingredient of mothballs:

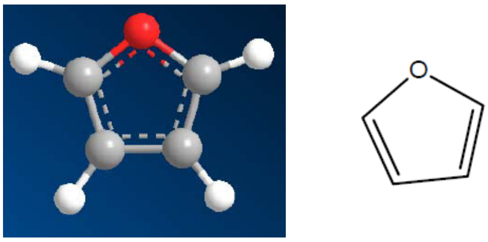


naphthalene (bicyclo[4.4.0]deca-1,3,5,7,9-pentene)

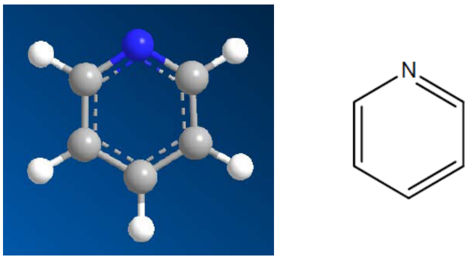
[4.4.0] indicates the carbon atoms in each part adjoining the interconnected section, i.e. 4 carbon atoms on each side and no additional carbons between the joining points, which may be known as the bridgehead carbons. The numbering is always given in descending order.

The name aromatic indicates the pungent odours of these substances. These mono- and polycyclic aromatic species can be substituted in the same manner as the alkanes etc. Another separate family of aromatics that need to be considered are the heterocyclic aromatics, which, by virtue of the inclusion of an element different to carbon into part of the ring, can have differences in electronegativity within the structure, affecting the reactivity.

Examples include furan, a 5-membered ring including oxygen and pyridine, a 6-membered ring including nitrogen. Some of these species make use of a lone pair of electrons from the heteroatom to contribute to the pi electron cloud.



furan



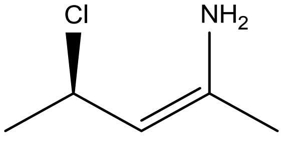
pyridine

Note how the heteroatom is indicated by its elemental symbol or colour, depending on the representation used. Hydrogen is always denoted by white, oxygen by red and nitrogen by blue, this will be similar for molecular modelling kits.

Stereochemistry – the formation of *cis* and *trans* isomers was discussed earlier and understanding the meaning of these terms can be essential in ensuring the correct raw materials are sourced or products made. Stereoisomers, or configurational isomers as they are sometimes known, have the same molecular formulae bonded in the same way but with the atoms occupying different locations in space. With the examples encountered previously, the direction of the bond was indicated by the line used, solid wedges indicating above the plane, dashed wedge below and solid lines in the plane of the page. *cis* and *trans* indicate the relationship of the groups to each other for simple alkenes with only two substituted groups, but it is also possible to indicate the stereochemistry of the atoms involved in these different orientations and to resolve issues of increased complexity.

There are two main methods used, known as the Cahn-Ingold-Prelog rules, depending on whether two molecules are geometric or configurational isomers. As stated, each stereogenic centre, previously known as a chiral centre, is assigned a letter to indicate the relative position of its substituents with relation to their relative priority, based on atomic number. After assigning priority to all substituents, hold the molecule so that the lowest priority group points away from you and look at the direction of motion with respect to highest to lowest priority for the remaining three groups. The letter *R* indicates a clockwise rotation from highest to lowest priority (from the Latin word rectus meaning right) and *S* (from the Latin word sinister for left) means an anti-clockwise rotation.

cis and *trans* denotation works for simple linear chains but this no longer works if there are two groups attached at either end of a double bond, i.e. four substitutions. For this situation, consider each carbon in the double bond separately. Assign the priorities of high and low to each pair of substituents, and then determine whether both low priority groups are on the same or different sides of the double bond. If they are on the same side, this is called a Z-alkene (from the German word zusammen meaning together); if they are on different sides, this is called an E-alkene (from the German word entgegen meaning opposite). The position of the centre assigned is given numerically e.g. (2Z,4R)-2-amino-4-chloro-2-pentene:



Note that numbering starts at the right hand of the molecule, moving towards the left.

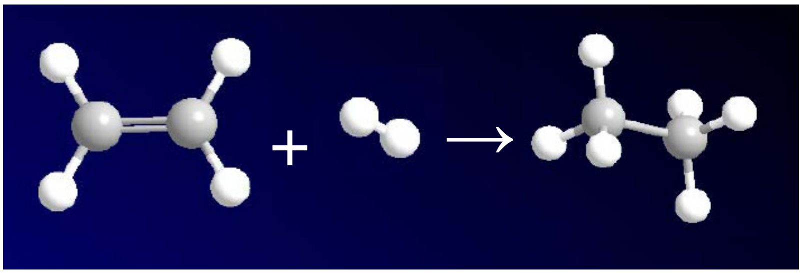
Organic acids and bases

Organic molecules can often act as weak acids or bases, donating or accepting protons, respectively. An example of an organic weak acid is ethanoic acid and a weak base would be ammonia. They are weak in strength as their ionization is very incomplete. The strengths are given, quantitatively, by pK_a and pk_b values for acids and bases, respectively, and the smaller the number the stronger the acid/base. In both cases the strength is related to the stability of the ion formed by proton loss or acceptance. For acids, the strength of the bond broken influences the value and for bases it is the ease with which the hydrogen ion is picked up by, for example, a lone pair.

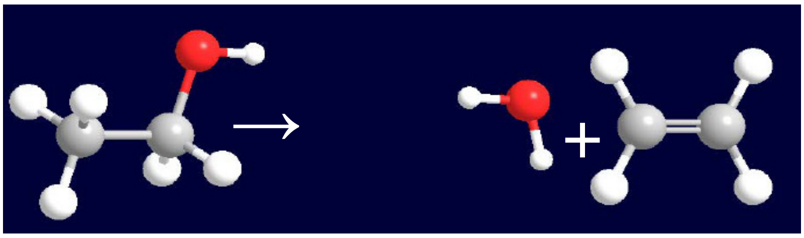
Main reaction types

Within organic chemistry there are several main reaction types, which are outlined below:

Addition reactions occur when two molecules combine to form another, larger molecule, and this involves at least one molecule with a multiple bond or unsaturated heteroatom. An example is the addition of hydrogen, called hydrogenation, of ethane to ethane:



Elimination processes involve the removal of two substituents from a molecule in either a one (E_2) or 2 (E_1) step reaction. An example is the removal of water, called dehydration, from ethanol to produce ethane:



When a functional group in a chemical structure is replaced by another, different functional group, this is known as a ***substitution reaction***. Classification can be made depending on whether the species bringing about the substitution is an electrophile (*electron loving*), either a positively charged species or a Lewis acid, or nucleophile, (*nuclear loving*) an electron-pair donor or Lewis base, as well as considering whether the intermediate species formed is a carbocation, a cation containing a positively charged carbon atom (C^+), carbanion, an anion containing a negatively charged carbon atom with an unshared electron pair (C^-), or free radical. The type of reaction is also affected by the type of reactant, i.e. aliphatic or aromatic.

Within ***nucleophilic substitution*** reactions there are two mechanistic variants, these being unimolecular nucleophilic substitution (SN_1) and bimolecular nucleophilic substitution (SN_2). SN_1 reactions involve two steps, where part of the molecule is displaced and a carbocation is formed, before the nucleophilic reagent reacts with the carbocation intermediate to form the reaction product, resulting in either inversion of configuration at the carbon centre or retention of the original configuration. The second reaction type, SN_2, has one step, with reagent attack of the carbon centre and ejection of the leaving group happening simultaneously. As a result of these concurrent process, SN_2 reactions always result in configuration inversion. When an aromatic substrate is involved in the reaction, it is known as nucleophilic aromatic substitution. ***Electrophilic substitution*** reactions are often associated with aromatic systems; however, for aromatics other than arenes, the reactions are more generally electrophilic addition.

The configuration of a molecule may also be altered by a ***rearrangement reaction***, where the carbon skeleton rearranges to form one of its structural isomers, often involving the transition of a substituent group from one molecule in the skeleton to its neighbour in an intramolecular rearrangement. Rearrangements can also occur intermolecularly. The movement of electrons in such transfers is not easily represented by traditional mechanistic drawings and is more likely a fluid transfer of electrons as opposed to the discrete nature inferred by the usual 'curly arrows' methods.

Basic thermodynamics

There are several basic terms that should be defined and understood before reading further about thermodynamic processes and variables; these include enthalpy, energy, internal energy, work and entropy.

Work

The work performed by a physical system is equal to the energy transferred to another physical system. This work can be mechanical, chemical, electromagnetic, gravitational or electrical but not heat, as this is treated separately in thermodynamics and both should be considered in energy transfer calculations although not both may be involved.

Energy

This is a scalar physical quantity, often defined as the ability of a physical system to do work on another physical system. Recall that work is the action of a force across a distance, energy is the ability to apply work vectors that act against natural forces.

Energy is measured in joules in the S.I. system, and the energy within a system cannot be created or destroyed but can be transformed from one form to another, according to the principle of conservation of energy (see first law of thermodynamics). It is noteworthy that the total energy of a system does not alter with time, only transfer, the value s only every relative to the reference state used. Energy is often stored in systems as matter, kinetic, electromagnetic or potential energy. Matter can be converted to energy and energy can be transferred by the transfer of matter, if an energy transfer occurs that is not due to matter transfer, then the receiving system changes as a result of work done on it as a result of the transfer. There is a limit to the efficiency of energy conversion between different forms (see second law of thermodynamics).

Internal energy

This is the total energy within a physical system, being the energy required to create the system but excluding the energy required to displace the systems environment, energy associated with a move or as a result of external forces. The internal energy is composed of contributions from kinetic and potential energy, and its value can be altered by heating the system or work done on the system, see first law of thermodynamics.

Internal energy is a state function and independent of path or process. It is measured in the S.I. unit of joules.

Enthalpy

This measures the total energy of a physical system, including internal energy and the energy needed to accommodate the system by displacement of the surrounding environment and forming the systems volume and pressure.

Enthalpy is a state function and the S.I. unit of measurement is the joule. It simplifies energy transfer descriptions, so is often used to describe changes in system energies as it also accounts for transfer to the environment, being the result of all non-mechanical work done on or by the system and any heat transfer.

Entropy

The entropy of a system quantifies the energy within the system that is unavailable for work in a thermodynamic process. Within some processes, such as energy conversion, which has a maximum efficiency, entropy accumulates within the system and is dissipated as waste heat.

It is a quantity that always remains constant or increases in an isolated system, as defined by the second law of thermodynamics, which provides an indication of whether a process is entropically favoured. As this quantity represents the spontaneous flow of heat from higher to lower temperature regions, hence, indicating the disorder within a system. As a result of this heat flux character, entropy is measured in joules per Kelvin in the S.I. system.

Zeroth law of thermodynamics

The zeroth law is a generalization of the principle that thermal equilibration exists within a number of bodies, or thermodynamic systems, that are in contact with each other. Thermal equilibrium exists when bodies or systems do not exchange heat. Thus, any two bodies (or systems) that are in thermal equilibrium with a third body (or system) must therefore be in equilibrium with each other. This implies that their temperatures are equal.

First law of thermodynamics

The first law of thermodynamics is basically the principle of the conservation of energy, stating that energy can neither be created nor destroyed, only transformed from one state of another. Within thermodynamics, it is considered that the change in internal energy of a system offsets the heat supplied to a system minus the work performed by the system on its surroundings. The law is developed from original statements made by Clausius, which initially presented the idea in terms of cyclic systems and then to internal energy, of processes that did not necessarily need to be cyclic, which is still the form used today. The law can be written as:

$$dU = \delta Q - \delta W$$

where dU is the change in internal energy; δQ and δW are the minuscule amounts of heat supplied to the system and work done by the system on its surroundings, respectively. It is worthy of note that many textbooks will have the sign in the above relationship as +, this is due to their consideration of δW as the work done on the system by its surroundings, and is the convention adopted by IUPAC. Also note that an exact differential is only used for internal energy as it is a state function i.e. independent of path, whereas the inexact functions used for work and heat are related to that fact they are dependent on the path taken to the final point. The expansion of an almost unchanging system, known as quasistatic, where any thermodynamic processes occur infinitely slowly, has a work function equal to the product of pressure (P) and volume change (dV), hence the change in internal energy becomes:

$$dU = \delta Q - PdV$$

It is worth noting that the functions of work and heat are energy changes that add or subtract energy from a system, whereas the internal energy is a property of the system, accounting for any energy exchanges performed on the system. This means that the same internal energy value can be determined for a variety of work and heat combinations.

The thermodynamic changes to a system, in terms of the first law of thermodynamics, can be divided into cumulative sections that are described as either adiabatic or isothermal diabatic.

Adiabatic processes are those that are thermally insulated, hence, any work exerted adiabatically on a given system results in the same final state of the system irrespective of how the work was performed, for example chemically, mechanically, electrically etc. This can be summarized as one of the statements resulting from the first law of thermodynamics: "*for all adiabatic processes between two specified states of a closed system, the net work done is the same regardless of the nature of the closed system and the details of the process.*"

This implies that internal energy is a state function, i.e. it is independent of the path taken to reach a particular point. As a result the internal energy changes from the initial reference point as a result of the work done:

$$U_A = U_0 + \Delta W_{0\to A}^{ad}$$

where, the adiabatic work done on the system from 0 to A is given by $\Delta W_{0\to A}^{ad}$. Following IUPAC convention we take as positive the work done on the system. As the reference state of U will be the same for any number of final states in the given system, it is possible to take a path from point A to point B, through the reference point, as the state function U will be independent of path taken, hence, the change in internal energy will be:

$$\begin{aligned}\Delta W_{A\to B}^{ad} &= \Delta W_{A\to 0}^{ad} + \Delta W_{0\to B}^{ad} \\ &= -\Delta W_{0\to A}^{ad} + \Delta W_{0\to B}^{ad} \\ &= -U_A + U_B = \Delta U\end{aligned}$$

Diabatic processes have related heat transfer components, as the non-adiabatic work done on the system is not equal to the change in internal energy change, and this must be taken into consideration in the balance of the system, as:

$$\Delta W^{non-ad} \neq \Delta U$$

Any diabatic change occurring at a constant temperature is known as isothermal diabatic, so the heat term will be at constant temperature (ΔQ^{iso}) and this allows an adiabatic work function to be used in the determination of the internal energy, hence:

$$\Delta U = \Delta W^{ad} + \Delta Q^{iso}$$

From this expression, it can be seen that the result of doing no work on a system that is thermally isolated results in zero change in ΔU, hence, the statement that '*the internal energy of an isolated system remains constant.*'

As mentioned previously, inexact differentials were used for the small amounts of heat and work within the system, however, it is possible to rewrite the equality with exact differentials by considering that work done, for reversible processes, is equal to the product of pressure (P) and the change in volume (dV), and that heat supplied is the product of temperature and the change in entropy, hence:

$$dU = TdS + PdV$$

The variables for which changes are measured or determined, i.e. volume, entropy and internal energy, are all state functions, hence, the derived equality, known as the fundamental thermodynamic relationship, is also true for non-reversible processes.

Second law of thermodynamics

Over an extended period of time, any differences in process variables, such as temperature, pressure and chemical potential, will equilibrate in an isolated system, this includes entropic terms and a system will tend to increase its entropy where possible, giving rise to irreversible processes. The second law of thermodynamics has several different versions:

The ***Clausius statement*** says that *'no process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature'* meaning that heat cannot flow from cold to hot regions without the use of external work.

The ***Kelvin statement*** says that '*no process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work*', which means that in the process of extracting heat energy from a high temperature source of energy with the aim to convert all the energy to work, some heat is lost.

The ***principle of Carathéodory*** states that '*in every neighbourhood of any state S of an adiabatically isolated system there are states inaccessible from S*', leading to the derivation of entropy and an initial insight into adiabatic accessibility, essentially defining a process as adiabatic if it exhibits a vanishingly infinitesimally small heat change over a given time.

Free energy

Any physical reacting system, at standard temperature and pressure, will aim to reduce its free energy, which is all the energy contained in a thermodynamic system that can be converted to work. This can be determined via either Helmholtz or Gibbs free energy.

Helmholtz free energy

A measure of the useful work that can be obtained from a physical system, at constant volume and temperature, is given by the negative of the Helmholtz free energy; the value reaching a minimum at equilibrium. The quantity is denoted by the letter *A* and is measured in joules in the S.I. system. Helmholtz energy is related to the internal energy (U), temperature (T) and entropy (S), and defined as:

$$A = U - TS$$

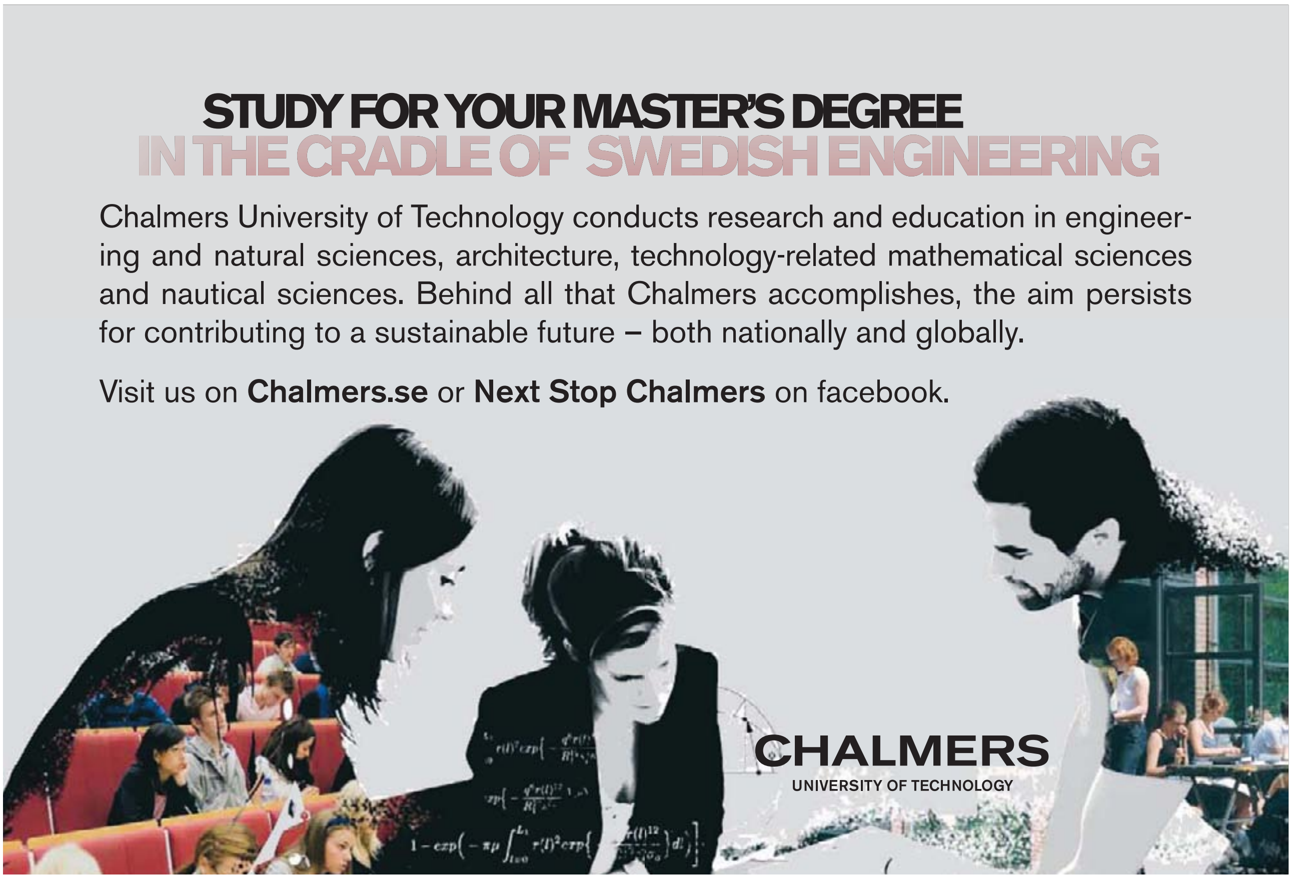
Gibbs free energy

This is a measure of the useful, non-mechanical, work that can be obtained from a physical system, at constant pressure and temperature, the maximum free energy being obtained for a reversible process. ΔG is minimised at system equilibrium, hence, allowing it to be used as an indicator of spontaneity for chemical reactions from this state. Gibbs free energy can be defined with respect to enthalpy (H), temperature (T) and entropy (S) as:

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

Where a negative value of ΔG implies that $\Delta S \geq 0$, hence, spontaneity is expected.

It should be noted that the Helmholtz and Gibbs free energy expressions deal with internal energy and enthalpy, respectively, making the Gibbs free energy function more useful to chemical engineers.



Kinetic theory of gases

In order to understand the kinetic theory of gases, it is essential to appreciate the terminology of the area and the underlying dynamics of the different phases of matter.

Solids

Within a solid material, the molecules are in very close proximity, contacting each other; the only permissible motion is that of vibration. The arrangement of molecules can be regular or random. In a regular system, the solid can be termed as crystalline depending on the length scale under study; for random packings, the solid is usually termed amorphous. These arrangements are held in place by interactions between the molecules, which can be a bond (ionic, covalent, metallic) or an electrostatic interaction (hydrogen bonds, van der Waals forces).

Liquids

In liquid systems, the molecules again contact but there will be occasional spaces in the structure; these spaces allow molecule movement through the system and a random arrangement results. Similar forces exist as in solid systems but the energy of the molecules themselves have more energy and are, hence, able to overcome these forces preventing a fixed arrangement. Generally, as a result of these spaces in the structure, the density of the liquid is a little less than that of the solid (water is a notable exception to this as solid ice floats on liquid water).

Gases

For gas systems, molecules have large, 10s of molecule scale, distances between them and are free to move. At usual temperatures and pressures, the intermolecular forces are practically negligible.

Phase changes

Solid to Liquid

If a heat is supplied to a solid, the vibrational energy will increase, allowing the molecules sufficient energy to adopt a less rigid arrangement and become a liquid, through a process known as melting. A specific amount of heat is required to convert one mole of a solid into a liquid and this is equal to the enthalpy of fusion. An inverse enthalpy of the same magnitude is evolved when a liquid becomes a solid, in the process of freezing, as the energy of the molecules reduces enough to allow the attractive interactions to arrange and bind the molecules into a solid form. The application of heat breaks the bonds within a system, and the formation of bonds, increasing order within the system, generates heat.

Liquid to gas

If sufficiently more heat is supplied to a liquid, this causes the molecules to increase their motion and relative speed, eventually breaking all the attractive forces binding them into a liquid form and producing a gas as the liquid boils. The inverse process is called condensation as the gas molecules reduce their energy sufficiently to condense into a liquid. The heat involved in the liquid-gas phase transition is called the enthalpy of vaporisation. Occasionally, some solid species form a gas on heating (or the reverse gas to solid on cooling), bypassing the phase of liquid, in a process called sublimation; the associated heat is known as the enthalpy of sublimation.

Once the molecules are in the gas phase, any increase in temperature translates into an increase in the thermal motion of the molecules themselves, hence, their average energy increases. In all systems, irrespective of phase, the caveat average is applied to physical parameters as that is exactly what is happening within the system. A plot of number of molecules against a given physical parameter will also show a distribution across the range and the easiest quantity to report is the average of this distribution. This means that some of the molecules will have less energy than the average whilst a proportion will have a greater energy. Within a liquid, this means that some molecules at the liquid-gas interface have a greater energy than the bulk liquid, which allows them to evaporate into the gas phase. Note that evaporation occurs at the interface between the two phases, not from the bulk liquid, as with boiling and the energy that escapes with the evaporating molecules is regained from the system surroundings. If the liquid-gas system is contained within a closed chamber, then the same process as above would occur at the liquid-gas interface, with evaporation of the liquid, at the interface into the gas phase, however, this time there is a similar reverse process that occurs where the gas molecules move within the container, interacting with the liquid surface at times, and some of the gas phase species with a low energy (compared to the average) will be insufficiently energetic to leave the surface again, condensing back into the liquid phase. The two processes continue and at some point the number of liquid molecules evaporating equals the number of gas molecules condensing, equilibrium is established within the system, where both process rates are equal. As with all equilibriums, this is a dynamic system and can be affected by a change in one of the system parameters.

Once equilibrium is established, at a set temperature, there will be a set number of molecules in the gas phase at any given point in time. These molecules will move within the chamber, striking the walls of the chamber and exerting a pressure, known as the saturated vapour pressure of the liquid. This pressure is temperature dependent.

Energy in chemical reactions

Before a chemical reaction can take place intra-molecular bonds of the reacting species must be broken and energy must be supplied to break these bonds. As discussed above, molecules within a system each have an energy associated with them. This energy is made up of contributions from several forms including: electric, chemical, thermal, vibrational, rotational and translational (kinetic) energy. The total energy of all the molecules in a system can be represented by the Maxwell-Boltzmann relationship, which is a law expressing the energy distribution among molecules at thermal equilibrium:

$$\frac{N_i}{N_j} = \exp\left[\frac{-\left(E_i - E_j\right)}{RT}\right]$$

Where N_x is the number of molecules with energy, E_x, R is the gas constant and T is absolute temperature. It can be see below that as the temperature increases so does the average energy of the molecules, as the kinetic energy of gas molecules is given by:

$$\frac{1}{2}mv^2 = \frac{3}{2}RT$$

In a reacting system, when the reactants collide energy is released and if energy is sufficient the bonds between the atoms break and reaction occurs. The minimum energy required for a reaction is known as the ***Activation Energy, E_A***, which is a fixed quantity, independent of temperature. The proportion of molecules with enough energy to react, governed by the Maxwell-Boltzmann distribution, rises exponentially with increasing temperature, explaining why a modest change in temperature results in a large change in reactivity.

Kinetic energy

Also known as translational energy, the kinetic energy of a molecule is the energy it possesses as a result of its motion. It is the energy required to accelerate the mass of the molecule from rest to the given speed, more correctly termed velocity as it is directional, hence a vector not scalar quantity. After being accelerated to the given velocity, the molecule maintains its kinetic energy till it changes velocity, which can, of course, mean the speed is maintained by the direction changes; any change in velocity results in a net gain or loss of energy to the molecule. Kinetic energy is relative within any given reference-frame for example a speeding car has kinetic energy relative to a stationary bystander but zero kinetic energy to an observer travelling at the same velocity. The kinetic energy of a molecule is given by:

$$E_{kin} = \frac{1}{2}\mathrm{mv}^2$$

Rotational energy

Also known as the angular kinetic energy of a molecule, the rotational energy is the kinetic energy resulting from the rotation of the molecule, and contributes to the total kinetic energy of the molecule. The rotational energy can be related to the moment of inertia (I) around the axis of rotation by:

$$E_{rot} = \frac{1}{2}\mathrm{I}\omega^2$$

where ω is the angular velocity. It is worth noting the similarity between the relationship for kinetic and rotational energies.

Vibrational energy

In a molecule with constant translational and rotational motion, the periodic motion of the atoms constituting the molecule is known as a vibration, each vibrational periodicity having a specific frequency. Generally, a molecule with N atoms has $3N - 6$ normal vibrational modes (a linear molecule would not demonstrate an observable rotation about its molecular axis, hence in such cases it reduces to $3N$-5, and diatomic molecules have only one normal vibrational mode due to symmetry). The vibrational modes can be excited when a molecule absorbs a quantum of energy that corresponds to the frequency of the vibration (v). The energy required is given by:

$$E = hv$$

where *h* is Planck's constant, 6.6261×10^{-34} J s. Adsorption of one quantum of energy, by a molecule in the ground, i.e. non-excited, state, excites a fundamental vibration. Adsorption of successive quanta of energy excite increasingly higher overtones of the molecular vibrations. The relationship between the amounts of energy required for successive vibrations to be excited is often approximated one additional quantum per overtone, as per the molecular vibrations obeying a simple harmonic model, however, vibration are actually anharmonic, meaning that successively less energy is required with each increasing overtone vibration after the fundamental. Eventually, sufficient energy will be adsorbed to dissociate the molecule.

The excitation of a vibrational mode results in an associated relaxation of the molecule back to its ground state by the emission of radiation, often in the visible or near-visible spectrum. As a result it is often easy to directly probe molecular vibrational transitions using spectroscopic methods, such as infrared (IR) or Raman.

IR spectroscopy requires a change in dipole for the molecule under study, a permanent dipole is not required merely a change in dipole moment. This is not necessary for Raman, For simple diatomics, there is only one bond, hence, one vibrational band. If the molecule is symmetrical, for example oxygen, there will be no change in dipole, so the vibration will be Raman, but not IR, active. In contrast, asymmetric diatomics, for example NO, are IR active. As the number of atoms, hence bonds, increases in a molecule, there will be an associated increase in the number of vibrational bands observed in the IR spectra and the complexity increases. Modes of vibration can include symmetric, asymmetric, stretching, rocking, scissoring, twisting and wagging.

Rotational energy

In addition to vibrational excitation of a molecule, giving rise to vibrational spectra, it is also possible to excite rotational modes within a molecule. Rotational modes arise from the symmetry present within a molecule, and rotationally active molecules must possess a dipole, such that there is either a difference in the centre of mass and the centre of charge for the molecule, or a separation of different charges on the same molecule. Spectroscopic methods studying rotational excitation only involve the use of microwave radiation and are confined to gases, which have quantised rotational excitations, as emissions are masked by collisions within solid and liquid systems. Gas molecules, such as diatomics, which have no inherent dipole can have induced dipoles as the result of excitation allowing spectra to be determined for those excited species.

Vibrational and rotational excitations usually occur concurrently within a molecule to give the vibration-rotation spectra, again usually obtained via either Raman or IR spectroscopy. As rotational transitions are weaker than vibrational transition, the former is often observed as fine structure on the latter. Such spectra can be useful in the determination of isotopic presence and abundances.

Physical properties of gases

The Gas Laws

The ideal gas law is essential to understanding the relationship between the key parameters of a gaseous system; the equation is underpinned by several other gas laws and students should have an appreciation of these as often their relatively simplistic relationships between parameters can be more useful than the full ideal gas law.

Boyle's Law (1661) – 'for a fixed mass of gas at constant temperature, the volume of the gas is inversely proportional to the pressure', which means that, for instance, a doubling of the volume of a system, with all other variables than volume constant, would halve the volume of the gas. This is expressed as:

$P \infty 1/V$ at fixed n and T

So $P{\cdot}V = \text{constant}$

Hence $P_1{\cdot}V_1 = P_2{\cdot}V_2$

This relationship should make sense by considering the case above. A container of volume V containing a set pressure of gas is increased in size to 2V, the gas molecules that were striking the walls of the container (V) produced pressure P as a result. As the volume increases (2V), the gas molecules will strike the walls of the container less frequently, as they have further to travel, meaning the pressure is reduced i.e. there is an inverse relationship where an increase in one parameter elicits a decrease in the other.

Charles' Law (1787) – *'for a fixed mass of gas at constant pressure, the volume of the gas is directly proportional to the Kelvin temperature'*, which means that, for instance, a doubling of the temperature, in Kelvin, with all other variables than volume constant, would double the volume of the gas as well. This is expressed as:

$$V \propto T \quad \text{at fixed n and P}$$

So $$V/T = \text{constant}$$

$$V_1/T_1 = V_2/T_2$$

It is important to remember that the temperature must be expressed in Kelvin.

This relationship is easy to comprehend, if one considers a fixed mass of gas in a container that has a zero-resistance moveable partition, for example a syringe. The barrier will adopt a position where the internal and external pressures are equal. Applying a temperature increase to the gas in the container (but not the external gas) will increase the speed of the molecules in the container, causing then to strike the partition more often, increasing the pressure; this will move the partition to a new position where the internal and external pressures are again equal. This movement will increase the volume of the system in response to an increase in temperature, and volume is proportional to temperature i.e. an increase in one parameter elicits an increase in the other.

Avogadro's Principle (1811) – builds on the Gay-Lussac Law of 1809 and states that *'the volume of a gas is directly proportional to the Kelvin temperature and mass of gas, and inversely proportional to the pressure'*. This combines both relationships from Boyle and Charles into one expression, including the number of moles of gas in the system. This is expressed as:

$$V \propto n{\cdot}T/P$$

So $$V{\cdot}P/n{\cdot}T = \text{constant}$$

$$P_1{\cdot}V_1/n_1{\cdot}T_1 = P_2{\cdot}V_2/n_2{\cdot}T_2$$

As for Charles' Law, it is important to remember that the temperature must be expressed in Kelvin. The constant that exists for this relationship is equal to R, the gas constant.

The Ideal Gas Law

The average molecular weight of a gas was met previously, and is useful when dealing with gas mixtures, enabling the number of moles to be calculated, hence, relating the behaviour of a gas mixture in terms of pressure, temperature and volume through the 'Ideal Gas Law'.

Experimentally it was found, as stated in Avogadro's Principle above, that:

$$P \cdot V \propto n \cdot T$$

The constant of proportionality is R, the Universal Gas Constant, and has several values depending on units, the most commonly used are 8.31415 J K^{-1} mol^{-1} or 0.082057 L atm K^{-1} mol^{-1}. Using the constant with all the other gas parameters gives the Ideal Gas Law:

$$P \cdot V = n \cdot R \cdot T$$

Where P is the pressure (N m^{-2}), V is the volume (m^3), n is the number of moles (mol), R is the Universal Gas Constant (J mol^{-1} K^{-1}) and T is the temperature (K). The Ideal Gas Law is the starting point for many applications and is derived from kinetic theory (see later)

From the Ideal Gas Law, it is important for chemical engineers to remember that for a fixed pressure and temperature the volume of a gas is proportional to the number of moles of the gas. This is useful when converting compositions between volume and molar bases.

The Ideal Gas Law is an equation of state, meaning it is dependent on the state of the species involved, not the route taken to attain the final state of the system, and describes the relationship between a quantity of gas and pressure, volume and temperature. From this relationship, it can be determined that, at standard temperature (273 K/0 $^{\circ}$C) and pressure (1.01325 x 10^5 N m^{-2}), 1 mole of gas occupies 22.4 litres.

Molar flowrate and the Ideal Gas Law

Similarly to the way mass and volumetric flowrates were related previously, it is also possible to relate volumetric and molar flowrates, using the Ideal Gas Law. In a completely analogous equation:

$$P\dot{V} = \dot{n}RT$$

Where P is the pressure (N m^{-2}), $\dot{V}$ is the volumetric flowrate (m^3 hr^{-1}), $\dot{n}$ is the molar flowrate (mol hr^{-1}), R is the Universal Gas Constant (J mol^{-1} K^{-1}) and T is the temperature (K). As mentioned previously, in chemical engineering volumetric flowrates are used extensively and the relationship between it and area or volume can allow the calculation of stream velocity, as:

volumetric flowrate (m^3 s^{-1}) = velocity (m s^{-1}) x area (m^2)

Mixtures of gases

An important aspect of gas mixtures is understanding the contribution of each component to the mix, this may be in considering air as a feedstock or mixed gas feeds to processes such as the Haber process, where ammonia is synthesized from nitrogen and hydrogen. The method of dealing with such multicomponent streams is by representing the contribution by a partial pressure for each gas species, this is underpinned by Dalton's law, which states that, for a mixture of perfect gases, the total pressure (P_{total}) of a given mixture is equal to the sum of the individual pressures (P_i) that each component alone would exert in the same container under the same conditions. Hence:

$$P_{total} = P_A + P_B + P_C + \cdots$$

The law is also applicable to real gases at low pressures where they exhibit ideal gas behaviour, but will be applicable in many cases that may be encountered during chemical engineering studies. For any gas, either perfect or real, in a mixture, the partial pressure (P_i) of the gas *i* would be given by:

$$P_i = x_i P_{total}$$

where x_i is the mole fraction of gas *i* within the gas mixture. The mole fraction can be found from the ratio of the number of moles of species *i* (n_i) compared to the total moles of gas (n_{total}) within the system, so that, the unitless mole fraction is given by:

$$x_i = \frac{n_i}{n_{total}}$$

It is useful to note that the sum of all the mole fractions within a closed system should, from the nature of their derivation, equal 1, i.e. the total system.

Equilibria and kinetics

There are two key pieces of information that chemical engineers wish to determine about any reactive system, firstly the final composition of the reaction mixture when the system has reached a stable point known as ***equilibrium*** and the time it will take to reach this point; these can be determined using ***chemical equilibrium thermodynamics*** and ***chemical kinetics***, respectively.

Equilibrium

Equilibrium is a dynamic state reached when the rates of the forward and reverse reactions, in a reversible reaction, are equal i.e. rate of product formation is equal to rate of destruction. At first, when only reactants are present in the system, there will be a fast rate of product formation and a slow rate of product destruction, as little product exists. Once the product concentration increases, so will the reverse reaction returning products to reactants. Hence, the forward reaction will tend to a limiting rate of reaction from a maximum and the reverse reaction will tend towards the same limiting rate of reaction from a minimum. When the two rates are equal, the maximum point of completion of the reaction at particular pressure and temperature has been established i.e. equilibrium; this point is quantified by the ***equilibrium constant***, K. If the value of K is very large, the reaction is said to go to completion.

Reaction kinetics

This determines at what rate the reaction will proceed towards the maximum extent. There are two main reasons for studying rates of reaction, to be able to predict how quickly a reaction mixture will move to its equilibrium state and understanding the rate of reaction can reveal the mechanism of a reaction. The rate of reaction can depend on a number of factors that can be controlled; these are temperature, pressure and/or the presence of catalyst(s). Depending on the aim of a reaction, a chemical engineer may be able to make the reaction proceed at an optimum rate. For example, it may be advantageous to make a reaction economical by proceeding very rapidly but not so rapidly as to produce an explosion.

The basic data required for the determination of chemical kinetics are the rate of change of products and reactants as a function of time. For example consider the reaction:

$$A + B \rightarrow C$$

The concentration of the species at any given time are [A], [B] and [C], respectively. The rate of reaction is equal to the rate of change of any species, so:

Rate of formation of product, C $= \dfrac{d[C]}{dt}$

Rate of destruction of reactant, A or B $= -\dfrac{d[A]}{dt} = -\dfrac{d[B]}{dt}$

Hence, in this case: $\dfrac{1}{c}\dfrac{d[C]}{dt} = -\dfrac{1}{a}\dfrac{d[A]}{dt} = -\dfrac{1}{b}\dfrac{d[B]}{dt}$

Any of these derivatives can serve as the definition of the rate of reaction, as one molecule of B must be destroyed for every molecule of A destroyed and in the process one molecule of C is formed. The complexity increases when we have stoichiometric coefficients that are not 1. This is easiest to consider with an example:

$$a\,A + b\,B \rightarrow c\,C + d\,D$$

With $\text{rate} = -\dfrac{1}{a}\dfrac{d[A]}{dt} = -\dfrac{1}{b}\dfrac{d[B]}{dt} = \dfrac{1}{c}\dfrac{d[C]}{dt} = \dfrac{1}{d}\dfrac{d[D]}{dt}$

When choosing the basis for stating the rate of reaction, it is important to state what species rate is chosen with respect to (A, B, C or D), to quote the chemical equation, thus avoiding ambiguity and keep the signs correct. Hence, the rate of reaction, for elementary reactions, is proportional to the concentrations of the reactants raised to some power, therefore, for the reaction above:

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = k\,[A]^a[B]^b$$

where k, the ***rate constant***, is independent of concentration but dependent on temperature. It should be emphasised that such convenient relationships between stoichiometry and rate do not always hold and that the rate equation is arrived at by experiment; the rate expression cannot necessarily be inferred by simply looking at the reaction equation.

Once a statement of the rate law is made, it allows a prediction of the rate, given the composition of a mixture and the experimental value of the rate constant. It shows a mechanism for the reaction, i.e. the way in which the molecules combine, and allows classification of reactions into various ***orders***.

Order – the order of a reaction is the power to which the concentration of a component is raised in the rate equation. hence, the ***overall order*** of a reaction is the sum of the powers of all concentrations. In the example above, the reaction would be a order in A, b order in B and (a+b) order overall.

Principal factors affecting rate of reaction

As stated above, the rate of reaction can be affected by concentration, temperature and/or the presence of catalyst(s)

Influence of concentration – this is described by the ***law of mass action***, which states that the rate of chemical reaction is proportional to the product of active masses of interacting substances, as shown above this active mass equates to the concentration of a species raised to the power of its stoichiometric coefficient. In a gaseous system the active mass is expressed using the partial pressure of each component instead of concentration

Influence of temperature – a rise in temperature usually results in a marked increase in reaction rate. The influence of temperature is often described by the ***Arrhenius equation***, which relates the rate constant, k to temperature:

$$k = Ae^{\left[-\frac{E_a}{RT}\right]}$$

where A is the frequency Factor, which is constant for any given reaction and has the same units as k, E_a is the activation energy, again constant for any given reaction (J/mol), R is the Universal Gas Constant (J/mol K) and T is the absolute temperature in K. A good rule of thumb for simple reactions is that the rate doubles for every 10 K increase in temperature.

Influence of catalyst(s) – catalysts can have a spectacular effect on rate of reaction, and in some cases the rate can be increased by up to a factor of 10^6. Catalysts can increase or decrease (hinder) the rate of a reaction but in most cases they are used to make a process faster and increase the economic efficiency of a reaction. The process works by lowering the activation energy required within the reaction system, and the catalyst(s) remains unchanged at the end of reaction but will participate in intermediate steps. It should be appreciated that the presence of the catalyst accelerates both the reverse and forward reactions so is has no effect on the final equilibrium position of the reaction, it just makes the reaching of that equilibrium quicker. In a multi reaction system, a catalyst may favour one reaction over any others, hence, increasing the yield of a desired product.

Determining chemical equilibrium

The equilibrium, also known as final, composition of a reaction mixture can be found using chemical equilibrium thermodynamics. For reactions that are irreversible there is only one reaction direction (reactants → products) and the concentration of the limiting reactant decreases as the reaction progresses eventually approaching zero. Eventually, in this case, could be seconds or years depending on the reaction. In this situation, the equilibrium composition corresponds to complete consumption of all of the limiting reactant. Other reactions are reversible, hence, reactants form products and products subsequently undergo reverse reactions to reform reactants. Such reversibility is commonly denoted by one of several symbols: $\leftrightarrow$ $\Leftrightarrow$ $\rightleftarrows$. In these systems equilibrium is reached at a certain point, remember that this equilibrium is dynamic.

To evaluate the equilibrium constant K, it is necessary to consider what is happening in the forward and reverse reactions, so again consider:

$$a\,A + b\,B \leftrightarrow c\,C + d\,D$$

The rate of the forward reaction is described by the law of mass action; hence, the rate is proportional to the product of the active masses of the interactive substances therefore:

$$\text{Rate}_{\text{forward}} = k_{\text{Forward}} [A]^a [B]^b$$

Similarly $\text{Rate}_{\text{reverse}} = k_{\text{Reverse}} [C]^c [D]^d$

At equilibrium $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{Reverse}}$

Thus $k_{\text{forward}} [A]^a [B]^b = k_{\text{reverse}} [C]^c [D]^d$

Therefore $\frac{k_{\text{Forward}}}{k_{\text{Reverse}}} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K$, the Equilibrium Constant

In general, K varies with temperature and does not vary with pressure.

Equilibrium constants of homogeneous liquid and gaseous systems

Consider a homogeneous liquid phase system, with known concentrations of reactants and products at equilibrium, the equilibrium constant is the ratio of the active masses of the products with relation to the active masses of the reactants. This shows that a larger value indicates greater product formation and the equilibrium constant is calculated from:

$$K_C = \frac{\text{concentration of products raised to power of their stoichiometric coefficients}}{\text{concentration of reactants raised to power of their stoichiometric coefficients}}$$

For example, consider the liquid phase reaction:

$$C_2H_5OH + CH_3COOH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Assuming that the initial volume of the solution is v and the initial moles are a moles of [C_2H_5OH], b moles of [CH_3COOH] and c moles of [H_2O]; recall that concentration is the quotient of moles by volume, the initial concentrations are:

[C_2H_5OH]	a/v
[CH_3COOH]	b/v
[$CH_3COOC_2H_5$]	--
[H_2O]	c/v

To express the equilibrium constant we require the concentration at equilibrium. Therefore, let α be the moles of alcohol, C_2H_5OH, reacted at equilibrium. So, carrying out a component balance using α and the reaction stoichiometry, the concentrations at equilibrium are:

$[C_2H_5OH]$	$(a-\alpha)/v$
$[CH_3COOH]$	$(b-\alpha)/v$
$[CH_3COOC_2H_5]$	α/v
$[H_2O]$	$(c+\alpha)/v$

Hence the equilibrium constant will be given by:

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} = \frac{\alpha(c+\alpha)}{(a-\alpha)(b-\alpha)}$$

Where Kc is unitless. The volume terms cancel out but this may not necessarily be the case depending on powers to which the concentrations are raised and the number of reactants and products.

Equilibrium constants of homogeneous liquid and gaseous systems

For gas phase systems, it is not possible to use the concentrations as for liquid systems, rather the concentration is expressed in terms of partial pressure raised to the power of the stoichiometric coefficient. Partial pressure being given by:

$$partial\ pressure, PP = y \cdot P_{total}$$

where y is mole fraction (unitless) and P_{total} is the total pressure, and for any gas phase equilibrium problem, pressure is always expressed in atmospheres (atm). The equilibrium constant, Kp is then calculated using:

$$K_p = \frac{partial\ pressure\ of\ products\ raised\ to\ power\ of\ their\ stoichioetric\ coefficients}{partial\ pressure\ of\ reactants\ raised\ to\ power\ of\ their\ stoichioetric\ coefficients}$$

For example, consider the gaseous phase reaction:

$$C_2H_{6\ (g)} \leftrightarrow H_{2\ (g)} + C_2H_{4\ (g)}$$

Determine an expression relating extent of reaction (α) to Kp.

Partial pressures of all reaction species, and the resulting active masses, are required to determine Kp, thus:

$$K_p = \frac{PP_{H_2}PP_{C_2H_4}}{PP_{C_2H_6}} = \frac{\frac{\alpha}{1+\alpha}P_T\frac{\alpha}{1+\alpha}P_T}{\frac{1-\alpha}{1+\alpha}P_T} = \frac{\alpha^2}{1-\alpha^2}P_T$$

Using the reaction stoichiometry, stoichiometric feeds and defining the extent of reaction, α, as the moles of C_2H_6 reacted at equilibrium, it is possible to write a component balance for the reaction:

	initial moles	equilibrium moles	y at equilibrium
C_2H_6	1	1 -α	(1 – α)/(1 + α)
H_2	0	α	α/(1 + α)
C_2H_4	0	α	α/(1 + α)
	total	1 + α	

Substituting in the expressions developed for each component, it then follows that Kp is represented by:

$$Kp = \frac{\left(y_{H_2}\cdot P_{total}\right)\times\left(y_{C_2H_4}\cdot P_{total}\right)}{\left(y_{C_2H_6}\cdot P_{total}\right)} = \frac{\left(\frac{\alpha}{1+\alpha}\right)\cdot Ptotal\times\left(\frac{\alpha}{1+\alpha}\right)\cdot Ptotal}{\left(\frac{1-\alpha}{1+\alpha}\right)\cdot Ptotal} = \frac{\alpha^2}{1-\alpha^2}\cdot Ptotal$$

By having this expression for Kp in terms of α, it is possible, given a value for Kp to determine the equilibrium yield of each component in the system. As the value of Kp changes, the value of α will also change, altering the equilibrium composition.

Effect of reaction conditions on the equilibrium position

As mentioned previously, equilibrium is a dynamic state; such systems are in a state of flux and a small perturbation, in terms of a change in a system variable, will produce a different equilibrium point, altering the final composition of the product mixture. Such changes can be predicted.

Le Chatelier's Principle – *'if one of the conditions of a system in equilibrium be altered, the system will adjust itself in such a direction as to try and neutralise this change of condition.'*

Influence of temperature

The influence of temperature on equilibrium position is different for endothermic and exothermic reactions, and each must be considered in turn to understand the predicted response within these systems.

Endothermic reactions – these have a positive heat of reaction, indicating that they take in heat from their surroundings during the progression of the reaction. As a consequence, such reactions are favoured by a rise in temperature, and this will raise the of rate reaction by supplying more heat to the molecules to increase the number of collisions. Increasing the temperature of an endothermic system will cause the equilibrium to move in such a way as to tend to reduce the temperature again, which is for the system to absorb heat, this drives the forward reaction, as it requires heat to be supplied to it. Hence, there is a shift in equilibrium to the right, producing higher product concentrations. In summary: T↑ Equil→ α↑or T↓ Equil← α↓, where α denotes the extent of reaction i.e. the number of moles of one of the products produced at equilibrium.

Exothermic reactions – these have a negative heat of reaction, indicating that they give heat to their surroundings during the progression of the reaction. As a result, such reactions are favoured by a lowering of temperature, although this can result in a decrease in rate as the molecules have reduced energy and, hence, do not participate in as many collisions; this means that a catalyst is often employed to increase the rate of reaction while cooling takes place. Increasing the temperature of an exothermic system will cause the equilibrium to move in such a way as to tend to reduce the temperature again, which is for the system to absorb heat, this drives the reverse reaction, as the forward reaction requires heat to be taken from it. Hence, there is a shift in equilibrium to the left, producing higher reactant concentrations. In summary: T↑ Equil← α↓ or T↓ Equil→ α↑, with α as above.

Influence of concentration

This is easiest to understand by considering an example reaction:

$$A + B \leftrightarrow C + D$$

If an increased amount of A is fed in to the reactor, its concentration will increase relative to all the other species and the equilibrium will shift to the right so as to oppose the increased presence of A. Thus more A and B will be consumed and more C and D produced i.e. the yield with respect to B will be increased. This supports the theory of using excess inexpensive reagents to maximise the conversion of more expensive species. In summary: $[A]\uparrow$ Equil$\rightarrow$ $\alpha\uparrow$ or $[C]\uparrow$ Equil$\leftarrow$ $\alpha\downarrow$.

Influence of pressure

The effects of pressure are only significant for reactions involving gases due to the incompressibility of liquids and solids. Consider a gaseous reaction where the number of moles on the product side are less than the number of moles on the reactant side:

$$A + B \leftrightarrow C$$

The production of product (C) is accompanied by a decrease in volume, 1 mole as compared to 2 moles, and will, therefore, be enhanced by an increase in pressure. Remember that according to the Gas Laws, volume is inversely proportional to pressure, hence a decrease in volume results in an increase in pressure. In summary: $P\uparrow$ Equil$\rightarrow$ $\alpha\uparrow$ or $P\downarrow$ Equil$\leftarrow$ $\alpha\downarrow$.

Conversely, there may be a gaseous reaction system where the number of moles on the product side are greater than the number of moles on the reactant side, for example:

$$A \leftrightarrow B + C$$

The forward reaction is accompanied by an increase in volume, 2 moles as compared to 1 moles, and will, therefore, be enhanced by a decrease in pressure. As above volume and pressure are inversely proportional. In summary: $P\uparrow$ Equil$\leftarrow$ $\alpha\downarrow$ or $P\downarrow$ Equil$\rightarrow$ $\alpha\uparrow$.

A third case that must be considered is when there is no change in the number of moles going from reactants to products, so moles on RHS equal moles on LHS. In this case, the equilibrium position is independent of pressure, as there is no change in volume.

On occasion, an inert species may be added to the reactant mixture, at constant total pressure, i.e. the addition of the inerts volume does not cause a pressure change itself, but it does in fact have the same effect as decreasing the pressure of the system, as the partial pressures of the reactants are decreased and there will be a reduction in their mole fractions reducing the number of collisions, the same as decreasing the pressure of each reactant.

Liquids and solutions

As discussed in the previous chapter on physical properties of gases, liquids are one of the three states of matter, which has packing similar to a solid but with some spaces between the molecules, allowing them to move within the system. The ability of liquids to vaporise, and subsequently condense back to a liquid was also discussed, and is of great use in chemical engineering in the process of distillation.

Liquids

A liquid is a substance that has constant volume, hence a constant density, at a given temperature, but that can change its shape to suit the vessel of containment. In a liquid the position of the molecules is essentially fixed, with small intermolecular distances, thus it is difficult to compress a liquid, easier than for solids but the compression is considerably less than can be achieved for gases.

Vapour pressure

Similarly to gases, the molecular kinetic energy of any liquid is not a set value but rather varies around an average value for the distribution, as determined by Boltzmann's Law, where the greatest number of particles have this average energy.

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There are some molecules that have an energy lower than the average and another portion that have an energy in excess of the mean; these more energetic molecules may have sufficient energy to be able to overcome the intermolecular forces binding the liquid and, if they are at the liquid-gas interface, vaporize. In an open system, the molecules will evaporate; in a closed system they will strike the walls of the vessel, exerting a pressure, and losing energy. Some molecules will lose sufficient energy that they will be unable to stay in the gas phase, rather they will condense into the liquid phase again. After a system defined period of time, the number of molecules evaporating will be equal to the number condensing, and vapour-liquid equilibrium is established. The final pressure exerted by the equilibrated system is known as the vapour pressure, which is temperature dependent. The volume of liquid and the volume above the liquid do not affect the equilibrium point and the same vapour pressure is achieved, hence, this is the vapour pressure of a given liquid at a given temperature. As the temperature increases, the kinetic energy of the molecules in the system increases, hence, increasing the pressure; the response of which follows a characteristic profile for each liquid with temperature.

Boiling point

From the scenario described above, an increase in temperature increases the vapour pressure of a liquid, until a point where bubbles of vapour form in the bulk liquid and rise to the surface. The pressure inside the bubbles is equal to the sum of atmospheric pressure and the hydrostatic pressure resulting from the depth of the bubble in the liquid. The point where bubbles are produced vigorously within the system is called the boiling point. As the pressure of the bubbles is affected by atmospheric pressure, the boiling point is also affected by this parameter. At 1 atm pressure, the normal boiling point is achieved, if the atmospheric pressure is lower than 1 atm, the boiling point will be lower, as the vapour pressure required in the bubbles will be reduced, hence, a lower temperature will achieve the vapour pressure needed; similarly a higher than atmospheric pressure will increase the boiling point. The relationship between temperature and the boiling point is characteristic of each liquid, and can be used as a tool for characterisation of unknown liquids.

The boiling point can be affected by molecular weight, often increasing with molecular weight. The intermolecular forces binding a liquid must be overcome for it to form a vapour, and an increase in polarity of a compound, can increase these forces, hence the boiling point. The energy involved in transforming a given amount of liquid into a gas, at STP i.e. 1 atm and 0 °C, is known as the heat of vaporisation, and the converse process has an energy associated with it, when a given quantity of gas condenses to a liquid, known as the heat of condensation. The existence of a boiling point is a traditional concept for most materials but there are some substances that will slowly decompose with the application of heat before reaching their boiling point.

Distillation

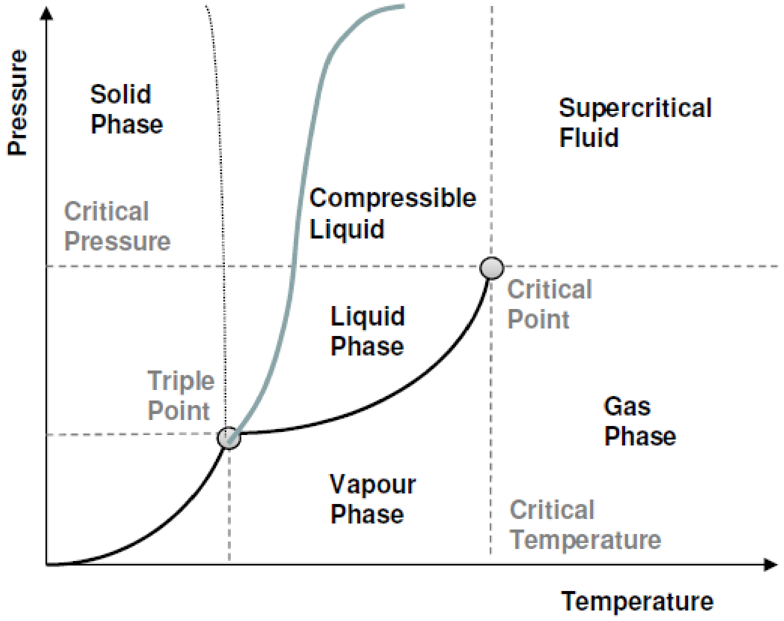
Chemical engineers are interested in vaporisation and condensation processes as these are important in distillation, which pervades chemical industry extensively. It is a common process for purification or separation of liquids, for example in the drinks, and oil and gas industries. The separation of a mixture of liquids, based on the differences in their boiling points, is known as fractional distillation.

Freezing point

Decreasing the temperature of a liquid, causes the average kinetic energy of the molecules within the system to decrease; this has the effect of decreasing the vapour pressure of the liquid, as there are fewer molecules with sufficient energy to break free of the bulk liquid. Further decrease of the liquid temperature, continues to reduce the translational motion of the molecules and there comes a point where the intermolecular forces will dominate within in the system, and the viscosity increases. At this point the liquid approaches the state of being solid and the molecules in some systems will orient into a rigid crystalline arrangement. At a given pressure, the change from liquid to solid will always occur at the same temperature, and at standard pressure (1 atm) this is called the freezing point. This temperature is generally considered to also be equal to the melting point of the solid back to a liquid.

Critical state

In order to be able to fully appreciate the concept of the critical state of a substance, it is essential to consider all three phases of the substance simultaneously, rather than as pairs as above, e.g. liquid-gas interchange. This is easiest to do by considering a ***phase diagram***. Here the substance is considered as being in a closed system with no interaction, such as heat loss or gain to other substances.



The figure above shows the phase diagram for water. A phase is any form of a substance, e.g. solid, and multiple phases can exist together in a system, with distinct boundaries between them. By considering a phase diagram, the equilibrium phase for any given pressure and temperature can be determined. Note the boundaries between phases, in the diagram, where both phases can occur and, most notably, the ***triple point***, which is where all three phases exist simultaneously. The conditions for the triple point are very specific, however, the solid, liquid and gaseous phases of a substance can all co-exist with their respective equilibrium processes.

Observe the figure above and how, by changing the temperature or pressure, it is possible to alter the phase of the substance. The effect of temperature has been addressed in the consideration of the three phases, with heat applied changing a solid to a liquid and then to a gas, and cooling reversing the process. The effect of pressure is also simply understood. Increasing the pressure on a gas or liquid system, will cause the system to act so as to reduce the volume of the substance, for a gas this is achieved by the compression to a liquid, the intermolecular spacing is reduced i.e. the volume is decreased. A similar scenario sees a reduction in volume going from liquid to solid. As may be anticipated, reducing the pressure will allow the substance to expand the intermolecular spacing changing solids to liquids, and liquids to gases. Mapping across from 1 atm on the pressure axis and seeing where it intersects the solid/liquid and liquid/gas boundaries gives the values for the melting and boiling points, respectively, at standard conditions.

The ***critical point*** is another specific point of note; this is where the gas phase created can no longer be compressed to become a liquid by manipulation of pressure alone. At a temperature below the ***critical temperature***, it is possible to condense a gas to a liquid. Above the critical temperature, it can be seen that there is no region for liquid along the pressure axis, increasing pressure merely compresses the gas, but it will never liquefy. This point is substance dependent and strong intermolecular forces increase the value of the critical temperature.

The final special point on the graph exists in the left-hand corner at the interface between the solid and vapour phases; at the exact conditions of pressure and temperature that make the dividing line, the solid and vapour will co-exist and ***sublimation*** will occur.

Solutions

In the phase diagram and discussion above, the existence of discrete phases, or phases in equilibrium with each other have been considered. However, an important class of system is the solution, consisting of two or more components, at least one liquid (solvent(s)) and materials that are dissolved within the solvent(s), known as solute(s). Solvents are commonly but not exclusively liquids, they can also be solids and gases that dissolve materials within themselves, these are known as disperse systems. Solutes can be solids, gases or liquids, even when the solvent is also a liquid. Their respective roles are defined by their relative quantities within the system, which can be a difficult point if these are quite similar.

The concentration of species within a solution is important to quantify and can be defined in terms of mass percent (the mass ratio of solute to solvent), molarity (mol L^{-1}) or molality (mol kg^{-1}). There is another important quantity associated with solutions; the vapour pressure, where the component vapour pressures are additive, as given by ***Raoult's law***, which is valid when interactions between molecules of the components of a solution are similar to the interactions between molecules of each component. These solutions are known as ***ideal solutions***. As discussed previously, there is a contrast between ideal and real gases, and the same is true for solutions. Real solutions show deviations from Raoult's Law, as a consequence of the differences in intermolecular interactions, but it can be a very useful tool, and the system will always tend towards the ideal as the mole fraction of one component approaches one or zero.

The addition of solutes to solvents also gives rise to changes in the colligative properties of the solutions compared to the bulk liquid, as discussed in the following Colligative Properties chapter.

Heat of Solution and Mixing

When a solid or gas dissolves in a liquid or when two or more liquids are mixed the attractive forces between molecules of feed material are overcome and new forces exist between neighbouring molecules of the product mixture or solution. These changes in intermolecular interactions are accompanied by the net absorption or release of energy, which results in internal energy and enthalpy differences between the pure compounds and the mixture. For ideal solutions, this effect is neglected and it is assumed that the specific enthalpy for a substance in a mixture is equal to the specific enthalpy for the pure substance, which is a good assumption for gas mixtures and liquid mixtures of similar compounds. For an ideal solution:

$$h_{\text{soln } T} = x_i h_i + x_j h_j$$

where x_i is the concentration of component I, which has specific enthalpy h_i, and x_j is the concentration of component j, with specific enthalpy of h_j. Hence, it follows that:

$$h_{solnT} = \int_{T_{ref}}^{T} x_i CP_i \, dT + \int_{T_{ref}}^{T} x_j Cp_j \, dT$$

So

$$h_{solnT} = \int_{T_{ref}}^{T} CP_x \, dT$$

where Cp_x is heat capacity of solution of concentration x and $Cp_x = x_i Cp_i + x_j Cp_j$

However, in some cases when two or more substances are mixed to form a gas mixture or to form a gas mixture or liquid solution there is an enthalpy change upon mixing: $\Delta H^{\ominus}_{soln}$ and this is called a ***non-ideal solution***. In a binary system, the enthalpy of any non-ideal solution can be defined as:

$$h_{solnT} = \int_{T_{ref}}^{25^{o}C} x_i CP_i \, dT + \int_{T_{ref}}^{25^{o}C} x_j Cp_j \, dT + \Delta H^{0}_{soln_{x25^{o}C}} + \int_{25^{o}C}^{T} Cp_x \, dT$$

Where $\Delta H^{\ominus}_{soln}$ is the enthalpy change per mole of a solute that is dissolved in a solvent, which varies with solution concentration x and must be found experimentally and the data is presented graphically or tabulated against solution concentration. There are components for heating the solution to the temperature where the standard heat is known, the enthalpy at that temperature and then heating to the final temperature. If $T_{ref} = 25\ ^{o}C$ then first two terms are eliminated, which is often the case:

$$h_{solnT} = \Delta H^{0}_{soln25^{o}C} + \int_{25^{o}C}^{T} Cp_x \, dT$$

The integral heat of solution ΔH_{soln} (T, n) is defined as the change in enthalpy when one mole of solute (gas or liquid) is dissolved in 'n' moles of liquid solvent at constant temperature T. As n becomes large, ΔH_{soln} approaches a limiting value, which is the heat of solution at infinite conditions. Often the values of ΔH_{soln} are tabulated in the literature at 25 ^{o}C and at different mole ratios: moles of solvent/moles of solute, so the value reaches a limiting quantity at infinite dilution.

Colligative properties

Colligative Properties

Colligative properties are those properties of a solution dependent on the number of molecules in a set volume rather than on the physical attributes of the molecules i.e. their relative molecular mass or molecular size. Such properties include osmotic pressure, elevation of boiling point, lowering of freezing point and relative lowering of vapour pressure. Alteration of such properties has consequences in processing and it necessary to be able to determine the direction and magnitude of an effect. It is also possible to use experimental measurements of colligative properties to i) determine relative molecular masses of non-ionised solutes, for example glucose, and ii) estimate the degree of ionisation of ionised solutes, for example salts.

Osmotic Pressure

The pressure that must be applied to a liquid/solution to prevent the flow of water across a semi-permeable membrane is known as the osmotic pressure. The transfer of water through semi-permeable membranes (cell walls), which can be selective, is important in biological systems, regulating concentrations. The same processes can be used in engineering applications to desalinate sea water.

There are two laws that govern the osmotic pressure of solutions, which state that osmotic pressure of a dilute solution is:

directly proportional to its concentration at constant temperature

directly proportional to its absolute temperature

It should be noted that osmotic pressure has the units of pressure, i.e. atm, bar, Pa etc., and that these laws are the analogues of the gas laws proposed by Boyle and Charles. This leads on to the analogous combined equation for ideal solutions, comparable to the ideal gas law:

$$\pi V = nRTi$$

where π is osmotic pressure (atm); V is volume (L); n is moles of solute (mol); R is the molar gas constant (L atm K^{-1} mol^{-1}); and T is absolute temperature (K); i is the van't Hoff factor.

Often simplified to: $\pi = \text{“i”}MRT$

Where M is Molarity (mol/L). Note, it should be evident that the number of moles of solute divided by the volume of solution in which the solute is contained is a molarity.

The van't Hoff factor is associated with the dissolution of the solute, and is determined from an equation utilising the ratio of the concentration particles produced on dissolution and the original concentration of the solute (n) and the degree of dissolution (α):

$$i = 1 + \alpha(n - 1)$$

For example NaCl dissociates into Na^+ and Cl^- as per:

$$NaCl \leftrightarrow Na^+ + Cl^-$$

For every mole of NaCl added to solution (LHS), there are two moles of particles produced (RHS), so the ratio (n) is 2/1 = 2, giving $i = 1 + \alpha$. This will alter depending on the solute and the degree of dissolution.

Relative Lowering of Vapour Pressure

Understanding and being able to determine the vapour pressure of a given mixture of different species is essential in separation processes and is an important aspect of membrane science. Concentration and vapour pressure, for ideal solutions, are related by Raoult's Law:

The vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and the mole fraction of the component present in the solution

This assumes that the chemical interactions between components of a mixed solution are the same as the bonding within the components making up the mixture.

Imagine a mixture containing components A and B, each component will have its own vapour pressure but when the two are mixed and have, most importantly, reached an equilibrium, the vapour pressure of the mixture will be a sum of the individual components, such that:

$$P_{mixture} = P_A X_A + P_B X_B$$

where P is pressure and X is mole fraction (unitless).

As the contributions from each component are related to the mole fraction of that component, increasing the number of species, hence total moles, will reduce the vapour pressure of each component. It also follows that dissolving a pure solute, with zero vapour pressure, i.e. it will not evaporate at the temperature of study, in a liquid, the vapour pressure of the mixture will be lower than that of the liquid alone.

Boiling and Freezing Points

The temperatures at which solutions boil or freeze can significantly alter the thermodynamic requirements of a process and need to be fully understood. Addition of solute to a liquid can alter both these parameters by differences in the vapour pressure of the resulting solution, for example adding salt to ice (water) in winter to lower its freezing point and clear icy roads.

Elevation of Boiling/Liquefaction Point (ebullioscopy)

The degree of elevation of boiling point (BPt) is proportional to the reduction of the vapour pressure of a dilute solution:

$$BPt_{solution} = BPt_{solvent} + \Delta T_{BPt}$$

And $$\Delta T_{BPt} = m \text{ x } K_{BPt} \text{ x } i$$

pm is molality (moles of solute with respect to mass of solvent, in mol kg^{-1}); K_{BPt} is the ebullioscopic constant (0.512 ^{o}C kg mol^{-1} for the boiling point of water); i is the van't Hoff factor (see osmotic pressure).

The boiling (or liquefaction) point of a given liquid (starting without solute) is achieved when an equilibrium exists between the liquid and gas phases. Equilibrium is a dynamic process, in the case of boiling point the rate of molecules evaporating from the liquid to the gas phase equals the rate of molecules condensing from the gas to liquid phase. The addition of a solute to the liquid acts to reduce the concentration of the liquid molecules, in turn reducing the evaporation of liquid to gas phase pathway in the equilibrium, as there is effectively less driving force in terms of liquid concentration as per Le Chatelier's principle. This means that more heat must be supplied to the system to drive the equilibrium, so the system boils at a higher temperature.

Suppression of Freezing/Melting Point (cryoscopy)

The degree of suppression of freezing point (MPt) is proportional to the reduction of the vapour pressure of a dilute solution:

$$\mathrm{MPt}_{\mathrm{solution}} = \mathrm{MPt}_{\mathrm{solvent}} - \Delta\mathrm{T}_{\mathrm{MPt}}$$

And $$\Delta\mathrm{T}_{\mathrm{MPt}} = m \times \mathrm{K}_{\mathrm{MPt}} \times i$$

Where m is molality (moles of solute with respect to mass of solvent, in mol kg^{-1}); $\mathrm{K}_{\mathrm{MPt}}$ is the ebullioscopic constant (1.86 °C kg mol^{-1} for the freezing point of water); i is the van't Hoff factor (see osmotic pressure).

The freezing (or melting) point, where an equilibrium exists between liquid and solid phases is usually reduced upon the addition of a solute, as compared to the pure solvent to which the solute is added. This is a result of the solute particles being unable to form part of the solid phase, as they are dissolved, so a lower proportion of the molecules in the solution contribute to the equilibrium. As equilibrium is a dynamic process, the system acts to re-establish equilibrium, which is when the rate of freezing becomes equal to the rate of melting i.e. the vapour pressures of the liquid and the solid in the system must be equal. This point is generally achieved at a lower temperature than for the pure solvent.

Chemical reactions

When dealing with chemical reactions there are several key terms that should be understood to allow full understanding of the process. The language has been developed in order to handle actual industrial chemical reactions. These definitions must be understood and are fundamental to the understanding of reaction variables.

Reaction terminology

Limiting reactant – this is the reactant that is present in the smallest stoichiometric amount. The limiting reactant determines the maximum extent to which a reaction can proceed, and if the reaction is 100 % complete then all of the limiting reactant is consumed and the reaction can proceed no further.

Excess reactant – refers to all other reactants within the process with exception of the limiting reactant. It is important to remember that the term may refer to more than one reactant.

Percentage excess (%XS) – this is based on the quantity of excess reactant above the amount required to react with the total quantity of limiting reactant according to the balanced chemical equation as per:

$$\%\ \text{XS} = \frac{\text{mols XS reactant - mols XS reactant required for completely react limiting reactant}}{\text{mols XS reactant required for completely react limiting reactant}} \times 100$$

The limiting and excess reactants, and associated percentage excesses are calculated from the feed quantities and reaction stoichiometry and give no indication of how much material has actually reacted at equilibrium.

Percent conversion – this is the percentage of any reactant that has been converted to products.

Degree of completion – refers to the percentage or fraction of the limiting reactant that has been converted to products.

Yield – for a single reactant and a product, the yield is the mass (or moles) of a chosen final product divided by the mass (or moles) of one of the initial reactants. If more than one product and more than one reactant are involved, the species on which the yield is based must be clearly stated. For example in $A + B \rightarrow C + D$, one possible yield expression would be number of moles of C/mole of A.

Initially to gain information about a system chemical engineers use *hypothetical* calculations, with information from the balanced stoichiometric chemical reaction To fully understand what is actually happening, the yield, degree of completion and percentage conversion need to be considered, where available. Such quantities are based on what is actually reacting in the system and what is produced.

In order to determine which quantity is limiting and which is in excess, the stoichiometric proportions (SPs) can be calculated using:

$$SP = \frac{feed\ amount}{stoichioetric\ coefficients}$$

The smallest SP determines the limiting reactant, meaning all others are in excess.

Extent of reaction α – when working with chemical reactions, it is useful to use the concept of extent of reaction to ease calculations. The extent to which a reaction proceeds (i.e. the material actually reacting can be expressed by) the extent of reaction (α) in moles. α conventionally relates the feed quantities to the amount of each component present in the product stream, after the reaction has proceeded to equilibrium, through the stoichiometry of the reaction. While the feed quantities are a useful tool in calculating extent of reacting, α can be based on any of the components, reactants or products, in the process. The maths involved is often easier if the component chosen has a stoichiometric coefficient of 1 itself but this is not always possible and, in some cases such as concurrent reactions, α has to be related to a term that appears in all reactions.

Ignoring the possibility of accumulation within a system, the balance for each reactant and product is generally:

output from reactor = (input in feed) – (consumption) + (generation)

All consumption and generation terms are expressed in terms of α, with consumption terms related to what is reacting (these are negative α terms) and generation terms related to what is produced (these are positive α terms). The representation of the amount of each species within a system is called a component balance.

Worked example – write a complete set of component balances for the following reaction:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

For each component the balance is: output = input – consumption + generation

Within this relationship all terms fit into either the consumption or generation category:

Consumption terms: SO_2 and O_2

Generation term: SO_3

The extent of reaction has to be defined in terms of one component only and this should be stated clearly. So in this example, let α = the moles of O_2 reacting α is a theoretical construct to assist in dealing with unknown quantities and should be treated in the same way in terms of proportionality as the stoichiometric coefficients in the fully balanced reaction equation. So in the same way that the number of moles of O_2 used can be calculated from the number of moles of SO_3 that is produced in a 1:2 ratio as they have stoichiometric coefficients of 1 and 2, respectively; it is straightforward to calculate that the same ratio holds for α, i.e. α moles of O_2 would react to produce 2α moles of SO_3.

Take each component in turn and apply a component balance using α and the balanced reaction stoichiometry, to give:

$(SO_2)_{out} = \quad (SO_2)_{in} - 2\alpha$

$(O_2)_{out} = \quad (O_2)_{in} - \alpha$

$(SO_3)_{out} = \quad (SO_3)_{in} + 2\alpha \qquad \text{But } (SO_3)_{in} = 0 \ \text{ so } (SO_3)_{out} = 2\alpha$

Such balances, when used with additional information, such as the yield and percentage conversion can allow unknown inputs and outputs to be determined. This is extremely useful when evaluating the expected equilibrium yield of a process and the effect that a change in the system conditions may invoke.

This approach, of using α to determine the composition of a system, is particularly useful when dealing with multiple reactions that occur simultaneously. This is best demonstrated with an example: in a reactor ethylene is oxidized to either ethylene oxide or carbon dioxide:

$$C_2H_4 + ½O_2 \rightarrow C_2H_4O \tag{1}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{2}$$

As stated above α can be based on any species in the reaction but close observation of the two reactions shows that only ethylene or oxygen occur in both reactions, hence, one of them should be selected. As the stoichiometric coefficients for ethylene are 1 in both reactions, it is best to select this as the basis of α. The reactions should also be labelled (as above) to identify their contributions to the overall process composition.

As there are two reactions occurring simultaneously, there needs to be two extents of reaction, one for reaction (1), α_1, and a second for reaction (2), α_2. Hence α_1 is the number of moles of C_2H_4 reacted in (1) and α_2 is the number of moles of C_2H_4 reacted in (2)

Combining the contribution of each reaction to the consumption of reactants and the generation of products, the component balances are:

$(C_2H_4)_{out} \quad = \quad (C_2H_4)_{in} - \alpha_1 - \alpha_2$

$(O_2)_{out} \quad = \quad (O_2)_{in} - 0.5\alpha_1 - 3\alpha_2$

$(C_2H_4O)_{out} \quad = \quad (C_2H_4O)_{in} + \alpha_1$ But $(C_2H_4O)_{FEED}=0$ so $(C_2H_4O)_{out} = \alpha_1$

$(CO_2)_{out} \quad = \quad (CO_2)_{in} + 2\alpha_2$ But $(CO_2)_{FEED} = 0$ so $(CO_2)_{out} = 2\alpha_2$

$(H_2O)_{ou\ t} \quad = \quad (H_2O)_{in} + 2\alpha_2$ But $(H_2O)_{FEED} = 0$ so $(H_2O)_{out} = 2\alpha_2$

As extent of reaction allows the determination of the number of moles of each species that are used or produced it also allows the evaluation of the masses of the output stream. This can be compared to the inputs and, as accumulation is being ignored, the result should be mass conservation, which is a useful check in such calculations.

Extent of reaction is a powerful tool in the determination of process compositions and provides a large amount of information to be elucidated for balances over unit operations.

Hess's law and temperature dependence of equilibria

Within chemical engineering, it is important to be able to understand whether a process gives out heat when a reaction occurs or whether there is a need to supply heat to the process. It is also useful to have some information about the magnitude of the energy involved. In order to achieve these two aims chemical engineers can calculate the heat of reaction (ΔH_R), but as this quantity varies with temperature, it is necessary to specify the conditions on which ΔH_R is based. Generally the Standard Heat of Reaction (ΔH°_R) is determined, this being the heat of reaction at standard conditions: 1 atm and 25 $^{\circ}$C. This requires the reactants and products to be taken in their standard state, i.e. the most stable phase at 1 atm and 25 $^{\circ}$C

Chemical reactions

When molecules collide, energy is released and, if this energy is sufficient then the reaction is activated and proceeds, this requires reactant bonds to be broken and product bonds to be formed. This results in either a net intake of energy (endothermic reaction, from the ancient Greek '*endo*' meaning internal) or a net release of energy (exothermic reaction, from the ancient Greek '*exo*' meaning external).

It is essential that designers of new chemical plants know how much heat each reaction generates or absorbs and that they make sure the plant can accommodate the net heat change. To enable them to do that, chemical engineers determine the ***heat (or enthalpy) of reaction***, which is used to express the amount of energy released into or absorbed from the environment. The heat of reaction is represented by ΔH_R.

Once calculated, the heat of reaction can provide a large amount of information. If the value is negative, then energy is released from the reaction system into environment, and the reaction is referred to as being exothermic. A positive heat of reaction, indicates that energy would be absorbed from environment into the system, and the reaction would be termed endothermic.

Industrial Chemical Reactions

It is common for large enthalpy changes occur in chemical processes, as said above for an endothermic process, heat is required from the surroundings so must be provided when working on a large scale, this sustains the reaction temperature and prevents the reaction rate from dropping. It is important to note, that sometimes the cost to provide heat to the reaction exceeds the cost of the reactants themselves, however, it may be worthwhile if the end product is sufficiently valuable.

Conversely, for an exothermic reaction, it is known that heat is given out by the system but it may be necessary to remove this heat in some cases by methods other than radiative heat loss from the reaction vessel. This is required to avoid a runaway reaction occurring and it is very common to remove heat from reactor using water, which has the benefit of producing 'heated' water that can be utilised elsewhere in plant, preventing waste.

As a consequence of these required measures, the heat of reaction can play an important role in the economics of a chemical process. Engineers must understand that industrial heats of reaction vary with temperature (covered in energy balances) but at low and moderate pressure, they are nearly independent of pressure. When determining the heat for any reaction, the process must be understood in terms of the stoichiometry of the reactants and products, as well as the state of aggregation (gas, liquid or solid) of all species involved in the reacting system. The state of matter of each component can significantly alter the heat of reaction value, for example the combustion of methane can have widely different values depending on the state of the water produced: 25 ^{o}C and 1 atm:

	ΔH_R at 25 ^{o}C and 1 atm
$CH_{4\,(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$	-890 kJ mol^{-1}
$CH_{4\,(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$	-802.3 kJ mol^{-1}

The difference of 87.7 kJ mol^{-1} is due to the fact that water is liquid in the first reaction and vapour in the second. This variance is associated with the heat of vaporisation of water at 25 °C and 1 atm.

Standard Heat of Reaction

As the heat of reaction, ΔH_R varies with temperature, it is necessary to specify the conditions on which ΔH_R is based, and it is usual to state ΔH_R at the ***standard conditions*** of 1 atm and 25°C. The heat is then referred to as the ***standard heat of reaction***, ΔH°_R, for which the reactants and products are taken as being in their standard state, i.e. the most stable state at 1 atm and 25°C.

As there are a multitude of chemical reactions, there will be a large number of associated ΔH°_R values, so it is not always possible or practical to list all the values of ΔH°_R values for every conceivable reaction. This is also unnecessary as it is sufficient to know information such as the ***standard heat of formation*** (ΔH°_f) or ***standard heat of combustion*** (ΔH°_C) for each compound involved in a reaction. Using the standard values for formation or combustion one of two methods of can be used to calculate ΔH°_R. One method is equation manipulation; the other is Hess's Law of Constant Summation.

Equation manipulation

This involves constructing formation or combustion reactions for the species contained in the overall reaction equation and manipulating these formation (or combustion) equations to satisfy the stoichiometry of the overall equation and ensure molecules appear on the reactant or product side as desired.

Worked example – using equation manipulation determine ΔH°_R for combustion of *n*-pentane.

Overall equation: $C_5H_{12\,(l)} + 8\,O_{2\,(g)} \rightarrow 5\,CO_{2\,(g)} + 6\,H_2O_{\,(l)}$

Formation reactions: $5C_{(s)} + 6H_{2\,(g)} \rightarrow C_5H_{12\,(l)}$ (1)

$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ (2)

$H_{2\,(g)} + \frac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)}$ (3)

Consulting the literature and obtaining formation heats (ΔH°_f) for each formation reaction:

(1) $5C_{(s)} + 6H_{2\,(g)} \rightarrow C_5H_{12\,(l)}$ $\Delta H^{\circ}_{R1} = \Delta H^{\circ}_{f1} = -173.0$ kJ/mol

(2) $C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$ $\Delta H^{\circ}_{R2} = \Delta H^{\circ}_{f2} = -393.5$ kJ/mol

(3) $H_{2\,(g)} + \frac{1}{2}\,O_{2\,(g)} \rightarrow H_2O_{\,(l)}$ $\Delta H^{\circ}_{R3} = \Delta H^{\circ}_{f3} = -285.84$ kJ/mol

The desired overall reaction is shown above and reference to it shows that it is necessary to reverse some equations and multiply others to get the required number of moles:

			ΔH_f / kJ mol^{-1}
-(1)	$5C_{(s)} + 6H_{2\,(g)} \rightarrow C_5H_{12\,(l)}$	= -1 x -173.0	+173.0
5 x (2)	$C_{(s)} + O_{2\,(g)} \rightarrow CO_{2\,(g)}$	= 5 x -393.5	-1967.5
6 x (3)	$H_{2\,(g)} + ½\,O_{2\,(g)} \rightarrow H_2O_{\,(l)}$	= 6 x -285.84	-1715.04
		Standard heat of reaction ($\Delta H^{\ominus}_R$) =	-3509.5 kJ mol^{-1}

As mentioned before this energy is only correct at standard temperature and pressure so any changes in either would need to be taken into account and a new value determined.

Hess's law of constant summation

The energies involved in the formation or combustion of the component species in a chemical reaction equation can be used, summatively, to evaluate the energy of the process as a whole, via the method of Hess's Law of Constant Summation. The values used in these calculations are standard heats of formation or standard heats of combustion.

Standard heats of formation – the evaluation of the standard heat of reaction, $\Delta H^{\ominus}_R$, from values of standard heat of formation, $\Delta H^{\ominus}_f$, can be summarised by the following equation:

$$\Delta H^{\ominus}_R = \Sigma\,[\Delta H^{\ominus}_f(\text{Products})] - \Sigma[\Delta H^{\ominus}_f(\text{Reactants})]$$

Using this notation is more convenient than stoichiometric formation equations. Importantly, elements are already formed so have no heat of formation associated with them, so should be excluded from calculations.

Worked example – using Hess's Law of Constant Summation determine $\Delta H^{\ominus}_R$ for combustion of *n*-pentane.

Overall equation: $C_5H_{12\,(l)} + 8\,O_{2\,(g)} \rightarrow 5\,CO_{2\,(g)} + 6\,H_2O_{\,(l)}$

$$\Delta H^{\ominus}_R = \Sigma\,(\Delta H^{\ominus}_f(\text{Products})) - \Sigma(\Delta H^{\ominus}_f(\text{Reactants}))$$

Ignore O_2 as elemental.

$$\Delta H^{\ominus}_R = [5(\Delta H^{\ominus}_f)\ CO_{2\,(g)}] + [6(\Delta H^{\ominus}_f)\ H_2O_{\,(l)}] - [(\Delta H^{\ominus}_f)\ C_5H_{12\,(l)}]$$

$$\Delta H^{\ominus}_R = [5 \times -393.5] + [6 \times -285.84] - [-173.0] = -3509.5 \text{ kJ/mol}$$

It is important to remember to include the stoichiometric coefficients and pay close attention to signs in mathematical evaluation.

Standard heats of combustion – thermochemical data is often also tabulated in the form of Standard Heats of Combustion, $\Delta H^{\ominus}_{C}$, which can also be used to calculate heats of reaction where:

$$\Delta H^{\ominus}_{R} = \Sigma\,[\Delta H^{\ominus}_{C}\,(\text{Reactants})] - \Sigma[\Delta H^{\ominus}_{C}\,(\text{Products})]$$

Similarly to the heats of formation there are some species that do not contribute to the heat of reaction calculation, in this case if any reactant or product are themselves combustion products, i.e. oxidised species, then the $\Delta H^{\ominus}_{C}$ term in the equation for that species is 0. The standard heats of combustion of any elements involved in the chemical reaction are not zero and must be included, i.e. they will combust.

The alteration in formula between the two standard heat sets originates from the algebraic manipulation of the combustion and formation reactions. Key substances appear on the LHS in combustion reactions as opposed to the RHS in formation reactions.

Considerations for thermochemical calculations

The conditions of phase and temperature must be closely observed in thermochemical calculations, ad this is particularly important for compounds such as water which can exist as more than one phase under common conditions. Variations in temperature must be accommodated through specific heat capacity and any changes in phase through latent heats, but usually the effect of pressure on the value of heat of reaction is small and can be considered negligible. Additionally, if there are excess reactants present in a reaction mixture, then the calculation should be based only on the amount of material actually taking part in the reaction.

Often the data provided for a calculation will be a mixture of heats of formation and heats of combustion, by understanding the underlying basis of the Hess approach it is possible to use such data to elucidate a required quantity. This is best demonstrated through an example.

Worked Example – calculate standard heat of reaction for the following reaction at 25 °C and 1 atm:

$$C_6H_{6\ (g)} + 3H_{2\ (g)} \rightarrow C_6H_{12\ (g)}$$

Using the following information

$\Delta H^{\ominus}_{f\ C_6H_6\ (g)}$	71.94 kJ/mol
$\Delta H^{\ominus}_{C\ C_6H_{12}\ (g)}$	-3949.2 kJ/mol
$\Delta H^{\ominus}_{C\ C\ (s)}$	-393.12 kJ/mol
$\Delta H^{\ominus}_{C\ H_2\ (g)}$	-285.58 kJ/mol

The best starting strategy is to assess what information is provided and what is missing. Close inspection of the formation heats provided, and application of:

$$\Delta H^{\ominus}_R = \Sigma\,[\Delta H^{\ominus}_f(\text{Products})] - \Sigma[\Delta H^{\ominus}_f(\text{Reactants})]$$

$$= [\Delta H^{\ominus}_f\,C_6H_{12\,(g)}] - [\Delta H^{\ominus}_f\,C_6H_{6\,(g)}]$$

shows that $\Delta H^{\ominus}_{f\ C6H12\ (g)}$ is unknown and requires calculation and application of the combustion heat version of Hess's Law allows this value to be determined:

First write formation the equation: $6C_{(s)} + 6H_{2\ (g)} \rightarrow C_6H_{12\ (g)}$

For this reaction note that $\Delta H^{\ominus}_R = \Delta H^{\ominus}_{f\,C_6H_{12}\,(g)}$

So $\Delta H^{\ominus}_R = \Sigma\,[\Delta H^{\ominus}_C(\text{Reactants})] - \Sigma[\Delta H^{\ominus}_C(\text{Products})]$

$$= [6 \text{ x } \Delta H^{\ominus}_C\ C_{(s)} + 6 \text{ x } \Delta H^{\ominus}_C\ H_{2\ (g)}] - [\Delta H^{\ominus}_C\,C_6H_{12\ (g)}]$$

$$= [(6 \text{ x } -393.12) + (6 \text{ x } -285.58)] - [-3949.2]$$

$$= -123 \text{ kJ mol}^{-1}\ C_6H_{12\ (g)} \text{ produced}$$

It is now possible to return to the original reaction and calculate $\Delta H^\ominus_R$:

$$\begin{aligned}\Delta H^\ominus_R &= \Sigma\,[\Delta H^\ominus_f(\text{Products})] - \Sigma[\Delta H^\ominus_f(\text{Reactants})]\\ &= [\Delta H^\ominus_f\, C_6H_{12\,(g)}] - [\Delta H^\ominus_f C_6H_{6\,(g)}]\\ &= [-123] - [71.94]\\ &= 195 \text{ kJ mol-1 } C_6H_{6\ (g)} \text{ reacted}\end{aligned}$$

Phase changes – when using standard heats of formation or combustion, it is essential that the phase of every component is known and taken into account, as any phase changes must be factored into the calculation. This is often the case for water:

$H_{2\ (g)} + ½O_{2\ (g)} \rightarrow H_2O_{\ (l)}$	$\Delta H^\ominus_{f\ H_2O\ (l)}$	-68.318 kcal mol^{-1}	–
$H_{2\ (g)} + ½O_{2\ (g)} \rightarrow H_2O_{\ (g}$	$\Delta H^\ominus_{f\ H_2O\ (g)}$	-57.798 kcal mol^{-1}	
$H_2O_{\ (l)} \rightarrow H_2O_{\ (g)}$	So, ΔH_V is	10.520 kcal mol^{-1} of H_2O changing phase	

Note the value for liquid water is more negative, i.e. more energy is released this is due to the heat given out by the system during the liquefaction of water vapour to liquid water, which itself has less energy – think about molecular motion in gases versus liquids.

Phase changes associated with solutions are probably less obvious but also need to be considered and factored into calculations. For example, the data provided may be for $\Delta H^\ominus_f$ HCl $_{(g)}$ but $\Delta H^\ominus_f$ HCl $_{(aq)}$ is desired, so it would be necessary to correct through the heat of solution, $\Delta H^\ominus_{soln}$ HCl $_\infty$, such that:

$½H_{2\ (g\ )} + ½Cl_{2\ (g)} \rightarrow HCl_{\ (g)}$	$\Delta H^\ominus_{f\ HCl\ (g)}$	-22.063 kcal mol^{-1}	+
$HCl_{\ (g)} \rightarrow HCl_{\ (aq)\infty}$	$\Delta H^\ominus_{sol\ HCl\infty}$	-17.960 kcal mol^{-1}	
$½\ H_{2\ (g)} + ½Cl_{2\ (g)} \rightarrow HCl_{\ (aq)\infty}$	$\Delta H^\ominus_{f\ HCl\ (aq)\infty}$	-40.023 kcal mol^{-1} HCl produced	

Strategies for dealing with thermochemical calculations

Firstly, it is important to write out a fully balanced chemical equation with stoichiometric coefficients and labelling species with the phases involved. Any phase changes must be taken into account with relation to the data being used. Using the reaction stoichiometry the heat of reaction can then be determined using one or more Hess relationships and paying particular attention to units of values used. Reporting the value, remember to state the species to which it relates and the molar quantity involved.

Variation of enthalpy with pressure

The effect of pressure variation on enthalpy can be considered to be negligible in applications involving changes of phase and significant changes in temperature.

Temperature dependence of equilibrium constant

The change in 'Gibbs Free Energy', $\Delta G^\ominus$ determines whether or not a chemical reaction will take place. For a chemical reaction to significantly proceed, $\Delta G^\ominus$ must be negative. We define $\Delta G^\ominus$ as:

$$\Delta G^\ominus = \Delta H^\ominus - T\,\Delta S^\ominus$$

where $\Delta S^\ominus$ is the entropy change of the reaction.

Also: $$\Delta G^\ominus = \Sigma\Delta G^\ominus_f\,(\text{products}) - \Sigma\Delta G^\ominus_f\,(\text{reactants})$$

The change in Gibbs free energy can also be related to the equilibrium constant, Kp in the following way:

$$\Delta G^\ominus = -\,RT\ln Kp$$

Note that Kp is always expressed in multiples of atmospheres, or is possibly unitless.

By combining these two equations, a direct relationship between temperature and equilibrium constant can be obtained:

$$\ln Kp_1 = -\frac{\Delta G_1^o}{RT_1} \text{ at Temperature } T_1 \qquad \& \qquad \ln Kp_2 = -\frac{\Delta G_2^o}{RT_2} \text{ at Temperature } T_2$$

$$\therefore\ \ln K_{P_1} - \ln K_{P_2} = \frac{\Delta G_2^o}{RT_2} - \frac{\Delta G_1^o}{RT_1}$$

$$\ln K_{P_1} - \ln K_{P_2} = \frac{\Delta H_2^o}{RT_2} - \frac{\Delta S_2^o}{R} - \frac{\Delta H_1^o}{RT_1} + \frac{\Delta S_1^o}{R}$$

When dealing with equilibrium calculations, it can often be assumed that $\Delta H^\ominus$ and $\Delta S^\ominus$ do not vary with temperature. Making this simplification:

$$\ln K_{P_1} - \ln K_{P_2} = \frac{\Delta H^o}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \text{or} \qquad \ln\frac{K_{P_1}}{K_{P_2}} = -\frac{\Delta H^o}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Giving the ***van't Hoff equation*** which describes the temperature dependence of the equilibrium constant. This equation is in keeping with Le Chatelier's principle. For example take an exothermic reaction, where $\Delta H^{\ominus}$ is negative, and increase the temperature. Raising the temperature means that T_2 is greater than T_1, so from the van't Hoff equation ln K_{P1} – ln K_{P2} is positive, meaning that ln K_{P1} is greatest, therefore, K_{P2} is smaller than K_{P1}. A reduction in Kp indicates a reduction in equilibrium yield. Equilibrium is shifted to the left, as expected by Le Chatelier's principle for the given system.

Material balances

Material balances are one of the topics that set chemical engineers apart from other engineers but it is essential to understand the underlying basic chemical principles. In order to perform balances it is important to categorise the process and all processes can be classified as one of batch, continuous or semi batch.

Batch processes – the feed is charged into the process system at the beginning of the process and all products are removed all at once some time later. No mass crosses the system boundary, excluding when the initial charge occurs and at the removal of the products at the end of process. Batch processes are generally used for small scale production and are operated in unsteady state. An example would be adding chemical reactants to a container, allowing the reaction to proceed to equilibrium and withdrawing the products once equilibrium has been achieved, as may be required when relatively small quantities are involved and/or the reaction is performed on a single occasion.

Continuous processes – the inputs and outputs flow continuously throughout the duration of the process. Such processes are more often used for large scale production and operated in either steady or unsteady state. An example would be the distillation of a mixture of liquids, feeding the liquids in to the bottom of the column, at a steady rate, and withdrawing the vapour from the top of the column also at a steady rate. In industrial applications, where large production rates are involved, often to increase profitability, the process is run as close to steady-state as possible.

Semi-batch (also semi-continuous) – this term is used to describe any process that is neither batch or continuous, incorporating processes where part of any reactant can be fed or part of any product removed during the process. An example would be allowing the contents of a pressurised gas container to escape to the atmosphere. As mentioned above these processes can be sub-classified as ***steady-state***, which occurs when all the variables in a process do not change with time and includes batch, continuous and semi-batch processes, and ***unsteady-state (or transient)***, which occurs when process variables change with time. This includes continuous processes.

General Mass Balance Equation

By understanding the flow of mass within a process system it is possible to determine whether scenarios such as leakage, fouling, absorption of reactants/products or erroneous measurement are occurring. This is best managed by performing a mass balances on the system; where the inputs and outputs are related to each other as per the General Mass Balance Equation (GMBE):

$$\text{input} + \text{generation} - \text{output} - \text{consumption} = \text{accumulation}$$

Where: input = all of the material that enters through the system boundaries
generation = all of the material that is produced within the system
output = all of the material that leaves through the system boundaries
consumption = all of the material that is consumed within the system
accumulation = all of the material that builds up within the system

This relationship assumes no nuclear reactions are involved and that the law of total mass conservation is obeyed. The general mass balance can be applied to several different types of balances, mainly ***total balances***, which are based on the total quantities of materials involved in the system i.e. the input and output masses; ***component balances***, where a balance is written for all individual substance using the GMBE in terms of extent of reaction; and ***element balances***, these are based on all atomic species in the reaction, as excluding nuclear reactions all atoms of an element entering the system must, in turn, be in the output stream. These balances can be written in one of two forms, either ***differential balances***, which indicate what is happening in a system at any given instant in time and each term is written as a ***rate***, per unit time e.g. kg/hr; or ***integral balances***, describing what happens between two instants in time, so that each term is an total amount e.g. kg.

For integral balances applied to simple batch, between their initial and final states, and differential balances applied to continuous steady-state processes the GMBE can be simplified, as accumulation is zero i.e. there is no build-up within system, so:

$$\text{input} + \text{generation} = \text{output} + \text{consumption}$$

When performing material balances it is always good practice to use a flowchart to keep account of all flows, this can be done for individual unit operations, which can then be added together to produce a ***Process Flow Diagram*** (PFD). Within the calculation, choose a basis that is suitable to allow material balances equations to be set up and solved for unknown variables, before feeding back into the flow chart, perhaps to supply information for another unit operation. Suitable bases would be that for a known mass fraction choose total mass or mass flowrate, and for a known mole fraction choose a total moles or molar flowrate basis.

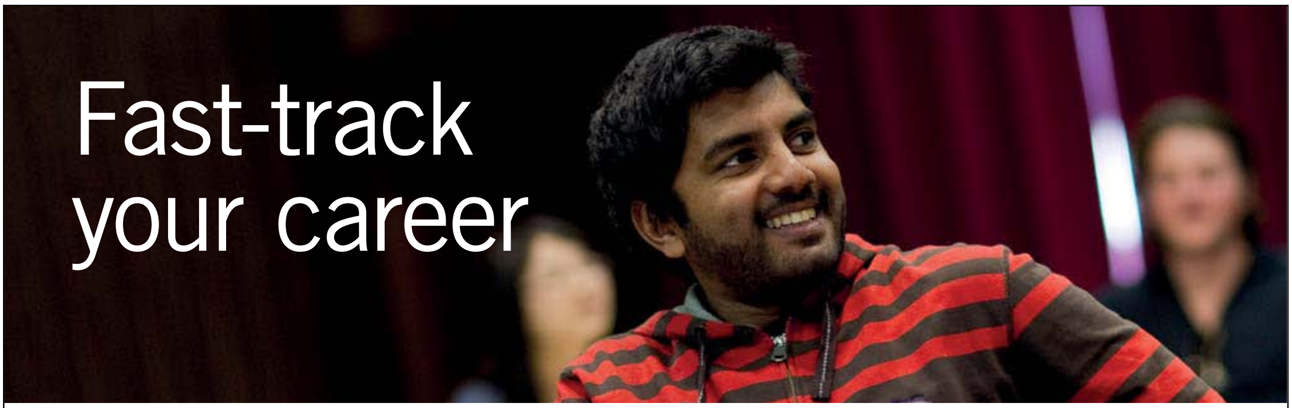
Drawing flowcharts

Flowcharts allow chemical engineers to keep a record of all flows within a system and may be annotated with lots of useful information. They provide details and values at a glance, organising information provided about a process in a convenient way that makes subsequent analysis and calculation easier. The most efficient method to draw a flowchart is the use of schematics and/or symbols to represent process units, such as reactors, mixers, separation units, etc., and lines with arrows to represent inputs and outputs, allowing material balance calculations to get started and keep them moving.

A flowchart must be fully labelled when started, with all known values for process variables and symbols for unknown variables being written for each input and output stream, providing a running tally for the problem solution, as each unknown variable is determined enter its value into the flowchart, thus producing a continuous record of where the solution stands and what must still be done. Often, algebraic symbols are assigned to unknown stream variables, for example m (kg solution/min), x (lb-mol N_2 /lb-mol), and n (kmol C_3H_8), and these variable names and their units are written on the flowchart

Common shortcuts that can simplify flow diagrams include using multiples of one unknown parameters where relationships exist, for example if the mass of stream 1 is known to be half that of stream 2, label the masses of these streams as m and 2m, rather than m_1 and m_2. Similar methods can be employed with mass fractions, for example the mass fraction of N_2 is 3 times that of O_2, hence label these mass fractions as y g O_2 /g and 3y g N_2 /g rather than y_1 and y_2. Within any diagram, the last mass or mole fraction to be labelled must be 1 minus the sum of all the others and when volumetric flowrates are given it is useful to label the stream with either the analogous mass or molar flowrate, since balances are not written on a volumetric basis.

m is always used to represent mass, n for moles, V for volume and the same symbols with dots above them represent the flowrates of these terms. x is use for the component fraction, as either mass or moles, in a liquid, while y would be the mole fraction in a gas mixture.



The methodologies outlined above can be used to both reactive and non-reactive systems, which have some subtle differences that are explained here.

Non-reactive systems

If no chemical reaction is taking place, this is called a non-reactive system, within which all balances are valid on a ***mass or mole basis*** where the generation and consumption terms are zero, hence:

$$\text{input} = \text{output}$$

Reactive Systems

As the name suggests, these are systems in which a chemical reaction takes place and there are several methods of calculation for reactive systems, being ***total balance***, which is valid on a mass basis only with generation and consumption terms equal to zero; ***element balance***, this is valid on a mass or molar basis and again the generation and consumption terms are zero; lastly, ***component balance***, where the stoichiometry is taken into account as well as the extent of reaction, so this has to be on a molar basis and generation and consumption terms have to be considered. For any of the three balances, the GMBE will always be applicable, even if some terms are subsequently neglected.

Combustion Reactions

This is a special class of a reactive system, where there is a rapid reaction of a fuel with oxygen and is probably more important than any other class of industrial chemical reactions but the combustion products are relatively worthless compared with the fuels burned to obtain them. The importance lies in the quantities of heat released during such reactions, used to produce steam to drive turbines that generate most of the world's electrical power. Chemical Engineers are heavily involved in analysing combustion reactions and reactors, and working towards the abatement and control of environmental pollution caused by these combustion products.

Combustion terminology – this is important to understand the processes occurring and communicate this to other engineers and colleagues. A ***fuel*** is required and will consist of coal, fuel oil, gaseous fuel, such as natural gas or liquefied petroleum gas. The fuel combusts to form carbon dioxide and carbon monoxide, from the carbon contained in it, and water, from the hydrogen content. When carbon monoxide is formed during combustion this is called ***incomplete combustion***. The common source of oxygen used in combustion reactions is ***air***, as it is cheap and readily available, and the output gases can be referred to as either ***stack gas***, which includes all gases that result from a combustion process including water vapour, so it is a wet basis, or ***flue gas***, reporting the gases that result from a combustion process not including water vapour, also known as a dry basis or Orsat analysis (a technique for stack gas analysis on a dry basis).

Within these output streams, for air reactions, one species will always occur and that is nitrogen, known as a ***tie element,*** material that passes through a system without change, depletion or addition. An important concept within chemical energy is the ***theoretical and excess air*** used in a reaction, this is due to the fact that in a reaction where one reactant is expensive it is practical to feed the less expensive reactant in excess to increase the yield of the valuable reactant at the expense of the cost of the excess reactants and addition of pumping costs. In combustion reactions air is inexpensive; therefore, combustion reactions are run with more air than needed to supply the oxygen required for the stoichiometric proportion to the fuel. The following terms are commonly used to describe the proportions of fuel and air to a reactor.

Theoretical oxygen – this is the number of moles (batch) or molar flow-rate (continuous) of oxygen needed for complete combustion of all the fuel fed to the reactor, assuming all carbon in fuel is oxidised to carbon dioxide and all hydrogen is oxidised to water.

Theoretical air – this is quantity of air that contains the theoretical oxygen.

Excess air – defined the amount by which the air fed to the reactor exceeds the theoretical air value, and the percentage excess air is:

$$\%\ Excess\ air = \frac{(\text{moles air})_{\text{feed}} - (\text{moles air})_{\text{theoretica l}}}{(\text{moles air})_{\text{theoretica l}}} \times 100$$

From this it is essential to remember that the theoretical air value is the air required for complete combustion of all fuel regardless of how far the reaction has proceeded. Confusion often occurs if this is forgotten, as the theoretical air required to burn a given quantity of fuel does not depend on how much is actually burning and the percentage excess air depends only on the theoretical air and the air feed rate, not how much oxygen is consumed in the reactor or whether combustion is complete or partial.

Material Balances on Combustion Reactions

The procedure is essentially the same as for any reactive system, however, the following additional points should be considered. When drawing and labelling flowcharts remember to include nitrogen at both the inlet and outlet, include unreacted fuel and unreacted oxygen at the outlet, and list all possible combustion products i.e. carbon dioxide, water and carbon monoxide. If several reactions occur simultaneously such as combustion to give carbon dioxide and carbon monoxide separate equations must be used for each reaction and element balances are the most appropriate balance. In contrast, for singular reactions component or element are both equally useful.

Energy balances

As a chemical engineer designing a process, one principal job would be to account for the energy that flows into and out of each process unit and determine the overall energy requirement of the system. This is done by writing an energy balance, which is performed in the same way as material balances, but rather than the mass flow to/from process, it is the energy flow. To calculate the energies generated or absorbed by each unit operation it is essential to understand the key underlying principles and concepts.

Heat capacity

The heat capacity of a substance is the amount of heat required to raise the temperature of a given amount of that substance by one degree. Hence, the units of heat capacity are energy per temperature per mass (or moles) e.g. cal g^{-1} $^{o}C^{-1}$ or kJ K^{-1} $kmol^{-1}$.

Sensible Heat and Heat Capacities

The heat that must be transferred to raise or lower the temperature of a substance, or mixture of substances, is known as the ***sensible heat*** and the quantity of heat required to produce a specified temperature change in a system can be determined from the ***First Law of Thermodynamics***, which states that '*the increase in the internal energy of a system is equal to the amount of energy added by heating the system, minus the amount lost as a result of the work done by the system on its surroundings*'.

The work done in a closed system, such as a batch process, is the change in internal energy, in contrast to the work done in an open system, including semi-batch or continuous, which is the change in enthalpy. This assumes neglect of kinetic (system stationary) and potential (no vertical displacement) energy and work (no moving boundaries). So to determine the sensible heat for a heating or cooling process, either the change in internal energy or the change in enthalpy need to be determined for the specified temperature change, as both of these quantities depend strongly on temperature. It should be noted that internal energy and enthalpy may be referred to as 'specific', meaning that they are quoted per unit mass. As a consequence, two considerations should be made, firstly variations in temperature at constant volume and, secondly, variations in temperature at constant pressure.

Constant volume systems – as the temperature is raised or lowered, the internal energy varies. The increase in internal energy represents the heat transferred to the substance at constant volume and the heat capacity at a constant volume is denoted by C_V and is related to internal energy by:

$$C_V = \left(\frac{dU}{dT}\right) \; at\ constant\ volume$$

Constant pressure systems – similar to internal energy, as temperature is raised or lowered, the enthalpy varies. The heat capacity at constant pressure is denoted by C_P and is related to enthalpy by:

$$C_P = \left(\frac{dH}{dT}\right) \; at\ constant\ pressure$$

The increase in enthalpy represents the heat transferred to the substance at constant pressure

'Specific' heat is sometimes used to denote heat capacity expressed on a per-unit-mass basis; C_P and C_V are physical properties and are tabulated in standard references. Most chemical industry processes do not involve material at a fixed volume but rather at a set pressure so C_P is more commonly encountered as a means of relating heat or energy input to temperature. Heat capacities are frequently expressed as polynomial relationships of the form:

$$C_P = a + bT \pm cT^2$$

Where the values of a, b and c are taken from the tables mentioned above. Conveniently, simple relationships exist between C_P and C_V. For liquids and solids C_P is approximately the same as C_V, and for an ideal gas C_P is equal to C_V corrected by the value of the gas constant, such that $C_P = C_V + R$. For non-ideal gases, the relationship is more complex and is not discussed here.

Change in Enthalpy

As chemical engineers often work with constant pressure systems, there is a need to be able to calculate the change in enthalpy or heat content of a substance, which is given by:

$$\Delta H = \int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_P dT$$

Note that if C_P is constant then the equation above simplifies to $\Delta H = C_P \Delta T$, which should be a familiar equation.

Within the relationship shown above, if the heat capacity is expressed in a polynomial form of the type: $C_P = a + bT + cT^2$, then:

$$\Delta H = \int_{T_1}^{T_2} (a + bT + cT^2) dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3)$$

Calculating enthalpy changes using mean heat capacities

It is sometimes convenient to use mean heat capacities to determine changes in enthalpy, and C_{Pm} is defined as follows:

$$C_{Pm} = \frac{H_2 - H_1}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C_P dT}{T_2 - T_1}$$

Thus the enthalpy of a substance at any temperature T can be calculated with respect to a particular reference temperature, T_R, using values tabulated in the literature at different temperatures. Each table is based on one particular reference temperature and all enthalpy calculations will relate to this particular reference temperature. Mean heat capacities can be used to calculate the enthalpy change involved in heating a substance generally from any temperature, T_a, to a second temperature, T_b:

$$\Delta H_{T_b - T_a} = C_{Pm T_b}(T_b - T_R) - C_{Pm T_a}(T_a - T_R)$$

Heat Capacity and Latent Heat Data for Different Substances

For greatest accuracy, wherever possible actual experimental heat capacities and latent heat data should be used in energy calculations. If information is not directly available, there are methods that may be used to estimate the data required, for heat capacities these include the Law of Dulong and Petit (solids), Kopp's rule (solids or liquids), the Fallon and Watson equation (liquid hydrocarbons) and the Ideal gas equation (gases); latent heat of fusion divided by the melting point equals a constant (2–3 for elements; 5–7 for inorganic compounds; and 9–11 for organic compounds); several methods are available to estimate the heat of vaporisation, including Trouton's rule, as the heat divided by normal boiling point equals a constant (21 for non-polar liquids, and 26 for water and lower alcohols), Kistyakowski equation (for non-polar liquids), Clausius-Clapeyron equation, reference substance plots, such as Duhrig plot, Othmer plot or Gordon plot, and lastly the Watson equation.

Enthalpy

Enthalpy is basically a measure of heat content and can be determined using heat capacities (covered above), however, enthalpy is not an absolute quantity and must be calculated relative to some chosen set of reference conditions and take any phase changes into account. So in enthalpy calculations, it is essential to state the reference conditions, including temperature and state.

Steam Tables

Over many years, the physical properties of water have been recorded in steam tables, serving as standard references for chemical engineers. The reference state of the tables is liquid water at 0 °C. When using steam tables to calculate enthalpies, these reference conditions should be observed or the values adjusted to comply with alternative reference conditions. As water is a common substance, the enthalpy of liquid water is well documented and any required values can usually be lifted directly from steam tables.

Any phase transition(s) taking place between the desired temperature and the reference temperature must take into account as latent heat(s) of the phase change(s). These corrections are added to the sensible heat changes calculated from the specific heat capacities, with contributions from the heat capacity calculation below the phase change and a second above it, such that:

$$h_T = \int_{T_R}^{T_P} C_{P_1} dT + \int_{T_P}^{T} C_{P_2} dT + LH$$

Where LH is the enthalpy associated with the change of phase, T_P is the phase transition temperature and C_{P_1} and C_{P_2} are the specific heat capacity contributions for the phases below T_P and above T_P, respectively.

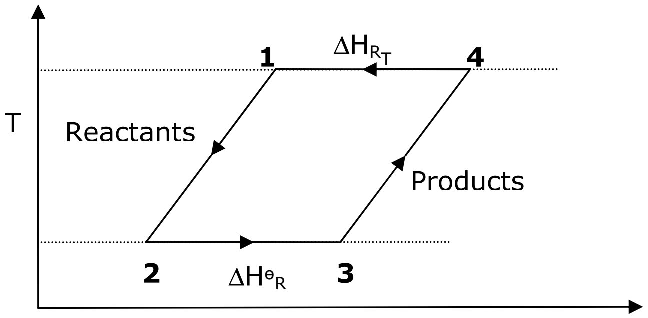
Enthalpy Changes Involving Chemical Reactions

Chemical reactions are associated with large enthalpy changes where energy is either released into or absorbed from the environment. The heat involved is called the heat of reaction (or enthalpy of reaction), and is denoted by ΔH_R. A negative value for ΔH_R indicates energy is released and the process is ***exothermic***, on the contrary a positive value assigned to ΔH_R denotes energy is absorbed and the process is ***endothermic***. Thus heats of reaction play a major role in economics of chemical processes. These heats can be calculated using Hess's Law of Constant Summation, which depends on the use of stoichiometric proportions of reactants fed in to the system at temperature (T) and pressure (P), that the reaction proceeds to completion, and that the products emerge at the same temperature (T) and pressure (P). For any calculations involving incomplete reactions (or excess reactants), ΔH_R should be based only on the amount of material actually taking part in the reaction. It has been mentioned previously, but is worth noting again that, at low and moderate pressure, ΔH^{e}_R, is nearly independent of pressure but importantly the value of heat of reaction depends on the states of aggregation of reactants and products.

It should also be noted that temperature has a marked effect on the heat of reaction, and the temperature dependence of the heat of reaction can be described by ***Kirchhoff's Law***, which is based on the fact that enthalpy is a ***state function***, hence, the final value of the heat of reaction is not a function of the route taken to evaluate it. This is best explained by an example, consider the reaction:

$$\text{Reactants} \rightarrow \text{Products}$$

Within an enthalpy pathway, the enthalpy change due to chemical reaction can be determined from either of two paths shown in the figure below: 1 → 4 or 1 → 2 → 3 → 4



So $$\Delta H_{R_T} = \Delta H_{\text{Reactants }(1-2)} + \Delta H^0_{\text{R }(2-3)} + \Delta H_{\text{Products }(3-4)}$$

$$\Delta H_{R_T} = \int_{T}^{T_{ref}} (aCp_A + bCp_B)\,dT + \Delta H^0_R + \int_{T_{ref}}^{T} (cCp_C + dCp_D)\,dT$$

$$\Delta H_{R_T} = \Delta H^0_{\text{R }(2-3)} + \int_{T_{ref}}^{T} Cp_{\text{Products}} - Cp_{\text{Reactants}}\ dT$$

ΔH_{RT} is obtained by calculating ΔH°_R using heats of formation and/or combustion, also calculating Cp(products) – Cp(reactants) from heat capacity polynomials provided, remembering to scale up according to stoichiometry, and integrating from T_{ref} to T over ΔCp.

Biography for Dr. Ashleigh Fletcher

Dr. Ashleigh Fletcher studied a first degree in Chemistry at the University of Durham (1997) before completing a PhD in adsorption science at the University of Newcastle-upon-Tyne (2000). After eight years of post-doctoral research in both chemistry and chemical engineering departments, with several high impact publications, she was appointed lecturer in chemical engineering at the University of Strathclyde, where she currently runs a thriving research group.