Essence of Chemical Engineering

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First Edition, 2012

ISBN 978-81-323-3049-3

Published by:
Research World
4735/22 Prakashdeep Bldg,
Ansari Road, Darya Ganj,
Delhi - 110002
Email: info@wtbooks.com

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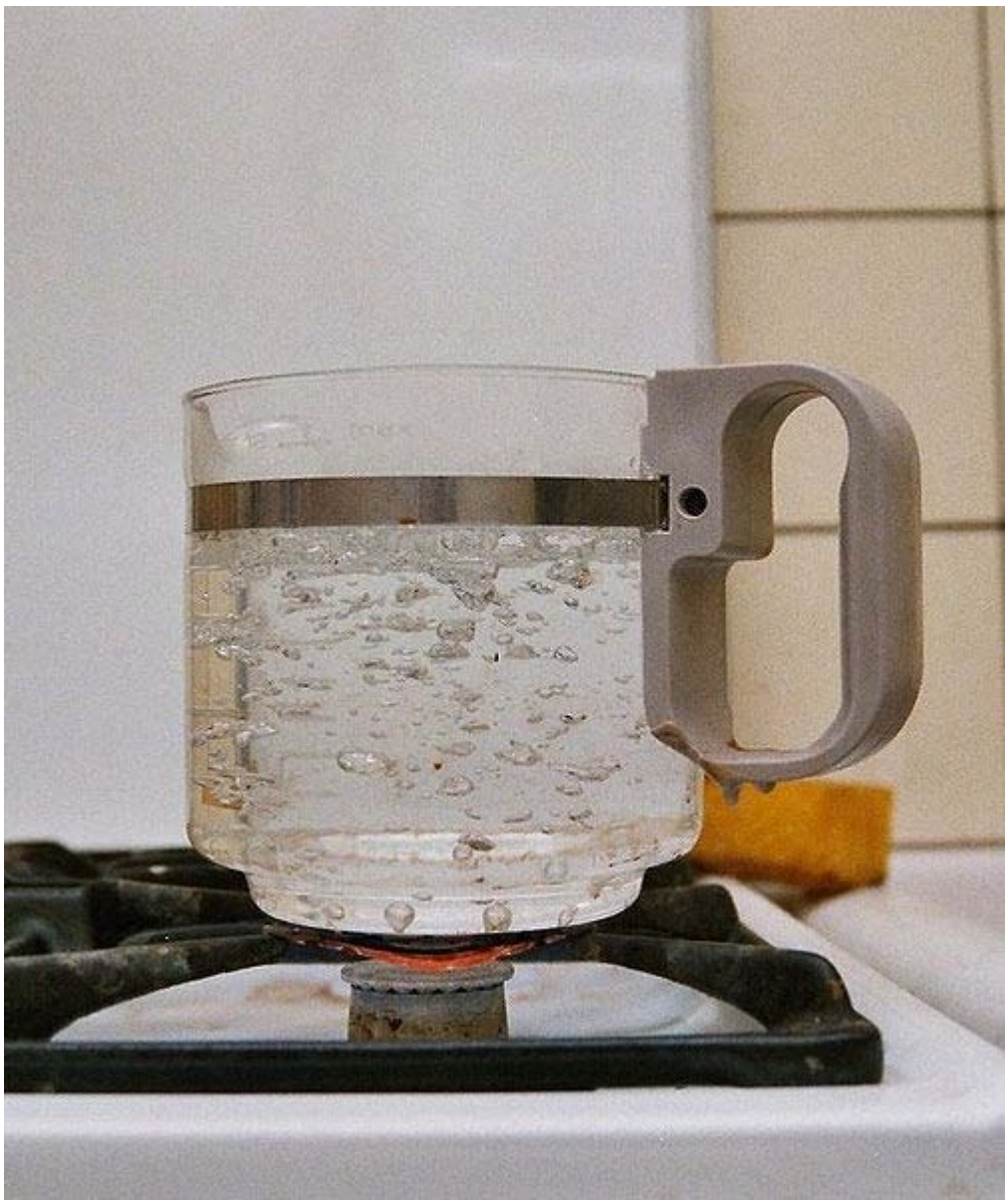
Chemical Substance

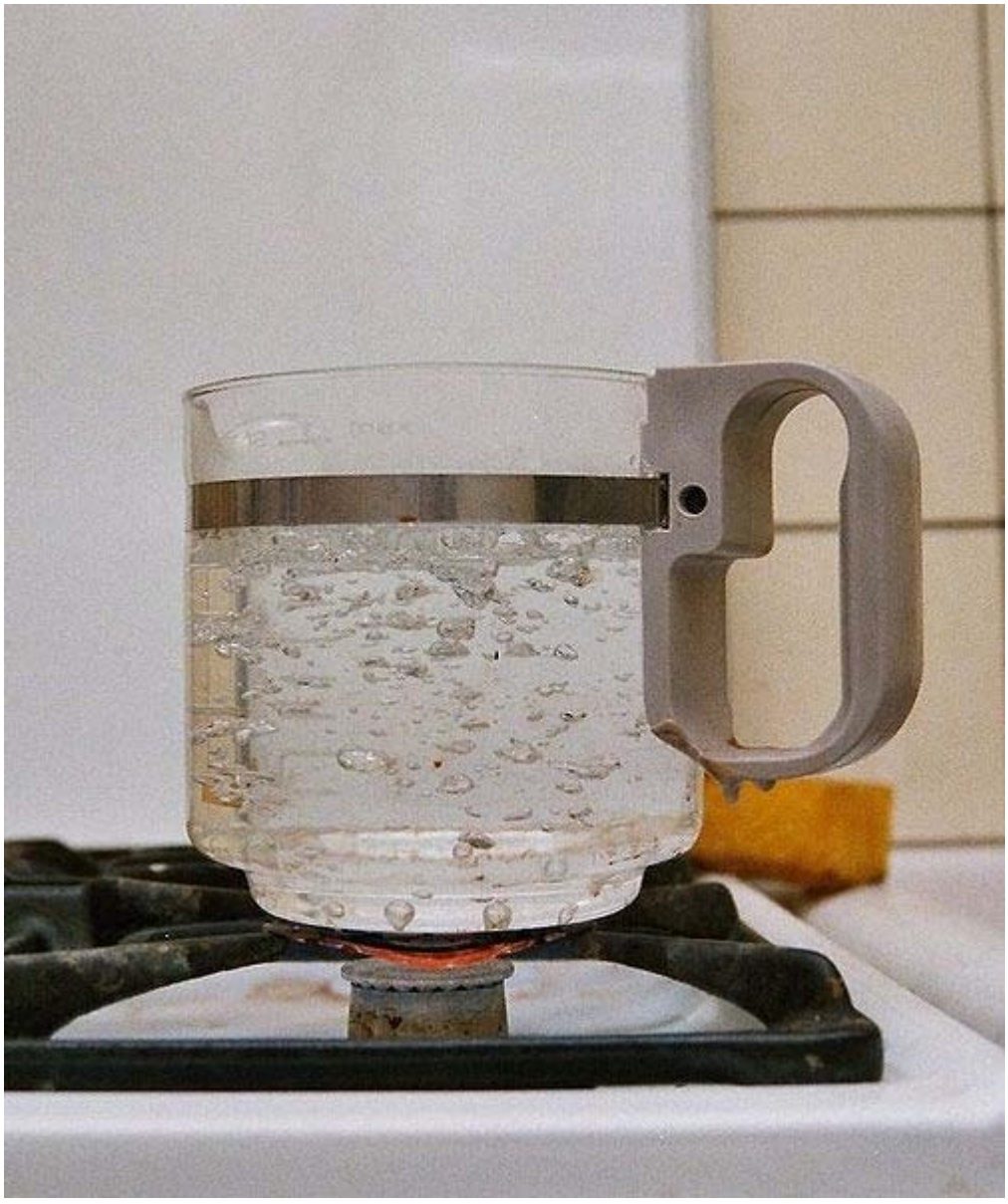


Steam and liquid water are two different forms of the same chemical substance, water.

In chemistry, a **chemical substance** is a form of matter that has constant chemical composition and characteristic properties. It can not be separated into components by physical separation methods, i.e. without breaking chemical bonds. Chemical substances are often called pure to set them apart from mixtures. A common example of a chemical substance is pure water; it has the same properties and the same ratio of hydrogen to oxygen whether it is isolated from a river or made in a laboratory. Other chemical substances commonly encountered in pure form are diamond, gold, salt (sodium chloride) and sugar (sucrose). Most chemical substances occur as mixtures with other chemical substances. For example, drinking water is a mixture of water, sodium chloride and many other chemical substances. Generally, chemical substances exist as a solid, liquid, gas, or plasma and may change between these phases of matter with changes in temperature or pressure. Chemical reactions convert one chemical substance into another.

Forms of energy, such as light and heat, are not considered to be matter, and thus they are not "substances" in this regard.

Definition



A colorful group of chemicals

Chemical substances (also sometimes referred to as a pure substance) are often defined as "any material with a definite chemical composition" in most introductory general chemistry textbooks. According to this definition a chemical substance can either be a pure chemical element or a pure chemical compound. But, there are exceptions to this definition; a pure substance can also be defined as a form of matter that has both definite composition and distinct properties. The chemical substance index published by CAS also includes several alloys of uncertain composition. Non-stoichiometric compounds are a special case (in inorganic chemistry) that violates the law of constant composition, and for them, it is sometimes difficult to draw the line between a mixture and a compound, as in the case of palladium hydride. Broader definitions of chemicals or chemical substances can be found, for example: "the term 'chemical substance' means any organic or inorganic substance of a particular molecular identity, including – (i) any combination of such

substances occurring in whole or in part as a result of a chemical reaction or occurring in nature"

History

The concept of a "chemical substance" became firmly established in the late eighteenth century after work by the chemist Joseph Proust on the composition of some pure chemical compounds such as basic copper carbonate. He deduced that, "All samples of a compound have the same composition; that is, all samples have the same proportions, by mass, of the elements present in the compound." This is now known as the law of constant composition. Later with the advancement of methods for chemical synthesis particularly in the realm of organic chemistry; the discovery of many more chemical elements and new techniques in the realm of analytical chemistry used for isolation and purification of elements and compounds from chemicals that led to the establishment of modern chemistry, the concept was defined as is found in most chemistry textbooks. However, there are some controversies regarding this definition mainly because the large number of chemical substances reported in chemistry literature need to be indexed.

Chemical elements

An element is a chemical substance that is made up of a particular kind of atoms and hence cannot be broken down or transformed by a chemical reaction into a different element, though it can be transmutated into another element through a nuclear reaction. This is so, because all of the atoms in a sample of an element have the same number of protons, though they may be different isotopes, with differing numbers of neutrons.

There are about 120 known elements, about 80 of which are stable – that is, they do not change by radioactive decay into other elements. However, the number of chemical substances that are elements can be more than 120, because some elements can occur as more than a single chemical substance (allotropes). For instance, oxygen exists as both diatomic oxygen (O_2) and ozone (O_3). The majority of elements are classified as metals. These are elements with a characteristic lustre such as iron, copper, and gold. Metals typically conduct electricity and heat well, and they are malleable and ductile. Around a dozen elements, such as carbon, nitrogen, and oxygen, are classified as non-metals. Non-metals lack the metallic properties described above, they also have a high electronegativity and a tendency to form negative ions. Certain elements such as silicon sometimes resemble metals and sometimes resemble non-metals, **and are known as** metalloids.

Chemical compounds

A pure chemical compound is a chemical substance that is composed of a particular set of molecules or ions. Two or more elements combined into one substance through a chemical reaction form a chemical compound. All compounds are substances, but not all substances are compounds.

A chemical compound can be either atoms bonded together in molecules or crystals in which atoms, molecules or ions form a crystalline lattice. Compounds based primarily on carbon and hydrogen atoms are called organic compounds, and all others are called

inorganic compounds. Compounds containing bonds between carbon and a metal are called organometallic compounds.

Compounds in which components share electrons are known as covalent compounds. Compounds consisting of oppositely charged ions are known as ionic compounds, or salts.

In organic chemistry, there can be more than one chemical compound with the same composition and molecular weight. Generally, these are called isomers. Isomers usually have substantially different chemical properties, may be isolated and do not spontaneously convert to each other. A common example is glucose vs. fructose. The former is an aldehyde, the latter is a ketone. Their interconversion requires either enzymatic or acid-base catalysis. However, there are also tautomers, where isomerization occurs spontaneously, such that a pure substance cannot be isolated into its tautomers. A common example is glucose, which has open-chain and ring forms. One cannot manufacture pure open-chain glucose because glucose spontaneously cyclizes to the hemiacetal form.

Substances versus mixtures

All matter consists of various elements and chemical compounds, but these are often intimately mixed together. Mixtures contain more than one chemical substance, and they do not have a fixed composition. In principle, they can be separated into the component substances by purely mechanical processes. Butter, soil and wood are common examples of mixtures.

Grey iron metal and yellow sulfur are both chemical elements, and they can be mixed together in any ratio to form a yellow-grey mixture. No chemical process occurs, and the material can be identified as a mixture by the fact that the sulfur and the iron can be separated by a mechanical process, such as using a magnet to attract the iron away from the sulfur.

In contrast, if iron and sulfur are heated together in a certain ratio (56 grams (1 mol) of iron to 32 grams (1 mol) of sulfur), a chemical reaction takes place and a new substance is formed, the compound iron(II) sulfide, with chemical formula FeS. The resulting compound has all the properties of a chemical substance and is not a mixture. Iron(II) sulfide has its own distinct properties such as melting point and solubility, and the two elements cannot be separated using normal mechanical processes; a magnet will be unable to recover the iron, since there is no metallic iron present in the compound.

Chemicals versus chemical substances

While the term *chemical substance* is a somewhat technical term used most often by professional chemists, the word *chemical* is more widely used in the pharmaceutical industry, government and society in general. Thus the word *chemical* includes a much wider class of substances that includes many mixtures of chemical substances that often find application in many vocations; and is most commonly used only for artificial or processed substances, such as the products of the chemical industry.

Artificial chemicals can be classified by production volume into bulk chemicals, fine chemicals and chemicals found in research only. Bulk chemicals are produced in very large quantities, usually with highly optimized continuous processes and to a relatively low price. Fine chemicals are produced at a high cost in small quantities for special low-volume applications such as biocides, pharmaceuticals and speciality chemicals for technical applications. Research chemicals are produced individually for research, such as when searching for synthetic routes or screening substances for pharmaceutical activity. In effect, their price per gram is very high, although they are not sold.

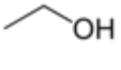
Naming and indexing

Every chemical substance has one or more systematic names, usually named according to the IUPAC rules for naming. An alternative system is used by the Chemical Abstracts Service (CAS).

Many compounds are also known by their more common, simpler names, many of which predate the systematic name. For example, the long-known sugar glucose is now systematically named 6-(hydroxymethyl)oxane-2,3,4,5-tetrol. Natural products and pharmaceuticals are also given simpler names, for example the mild pain-killer Naproxen is the more common name for the chemical compound (S)-6-methoxy-α-methyl-2-naphthaleneacetic acid.

Chemists frequently refer to chemical compounds using chemical formulae or molecular structure of the compound. There has been a phenomenal growth in the number of chemical compounds being synthesized (or isolated), and then reported in the scientific literature by professional chemists around the world. An enormous number of chemical compounds are possible through the chemical combination of the known chemical elements. At the last count, about thirty million chemical compounds are known. The names of many of these compounds are often nontrivial and hence not very easy to remember or cite accurately. Also it is difficult to keep the track of them in the literature. Several international organizations like IUPAC and CAS have initiated steps to make such tasks easier. CAS provides the abstracting services of the chemical literature, and provides a numerical identifier, known as CAS registry number to each chemical substance that has been reported in the chemical literature (such as chemistry journals and patents). This information is compiled as a database and is popularly known as the Chemical substances index. Other computer-friendly systems that have been developed for substance information, are: SMILES and the International Chemical Identifier or InChI.

Identification of a typical chemical substance

Common name	Systematic name	Chemical formula	Chemical structure	CAS registry number	InChI
alcohol, or ethyl alcohol	ethanol	C_2H_5OH		[64-17-5]	1/C2H6O/c1-2-3/h3H,2H2,1H3

Isolation, purification, characterization, and identification

Often a pure substance needs to be isolated from a mixture, for example from a natural source (where a sample often contains numerous chemical substances) or after a chemical reaction (which often give mixtures of chemical substances).

Chapter 2

Chemistry

Chemistry is the science concerned with the composition, structure, and properties of matter, as well as the changes it undergoes during chemical reactions.

During chemical reactions, bonds between atoms break and form, resulting in different substances with different properties. In a blast furnace, iron oxide, a compound, reacts with carbon monoxide to form iron, one of the chemical elements, and carbon dioxide.

Chemistry (the etymology of the word has been much disputed) is the science of matter and the changes it undergoes. The science of matter is also addressed by physics, but while physics takes a more general and fundamental approach, chemistry is more specialized, being concerned with the composition, behavior (or reaction), structure, and properties of matter, as well as the changes it undergoes during chemical reactions. It is a physical science which studies various substances, atoms, molecules, crystals and other aggregates of matter whether in isolation or combination, and which incorporates the concepts of energy and entropy in relation to the spontaneity of chemical processes.

Disciplines within chemistry are traditionally grouped by the type of matter being studied or the kind of study. These include inorganic chemistry, the study of inorganic matter; organic chemistry, the study of organic (carbon based) matter; biochemistry, the study of substances found in biological organisms; physical chemistry, the study of chemical processes using physical concepts such as thermodynamics and quantum mechanics; and analytical chemistry, the analysis of material samples to gain an understanding of their chemical composition and structure. Many more specialized disciplines have emerged in recent years, e.g. neurochemistry the chemical study of the nervous system.

Summary

Chemistry is the scientific study of interaction of chemical substances that are constituted of atoms or the subatomic particles: protons, electrons and neutrons. Atoms combine to produce molecules or crystals. Chemistry is sometimes called "the central science" because it connects the other natural sciences such as astronomy, physics, material science, biology and geology.

The genesis of chemistry can be traced to certain practices, known as alchemy, which had been practiced for several millennia in various parts of the world, particularly the Middle East.

The structure of objects we commonly use and the properties of the matter we commonly interact with are a consequence of the properties of chemical substances and their interactions. For example, steel is harder than iron because its atoms are bound together in a more rigid crystalline lattice; wood burns or undergoes rapid oxidation because it can react spontaneously with oxygen in a chemical reaction above a certain temperature; sugar and salt dissolve in water because their molecular/ionic properties are such that dissolution is preferred under the ambient conditions.

The transformations that are studied in chemistry are a result of interaction either between different chemical substances or between matter and energy. Traditional chemistry involves study of interactions between substances in a chemistry laboratory using various forms of laboratory glassware.

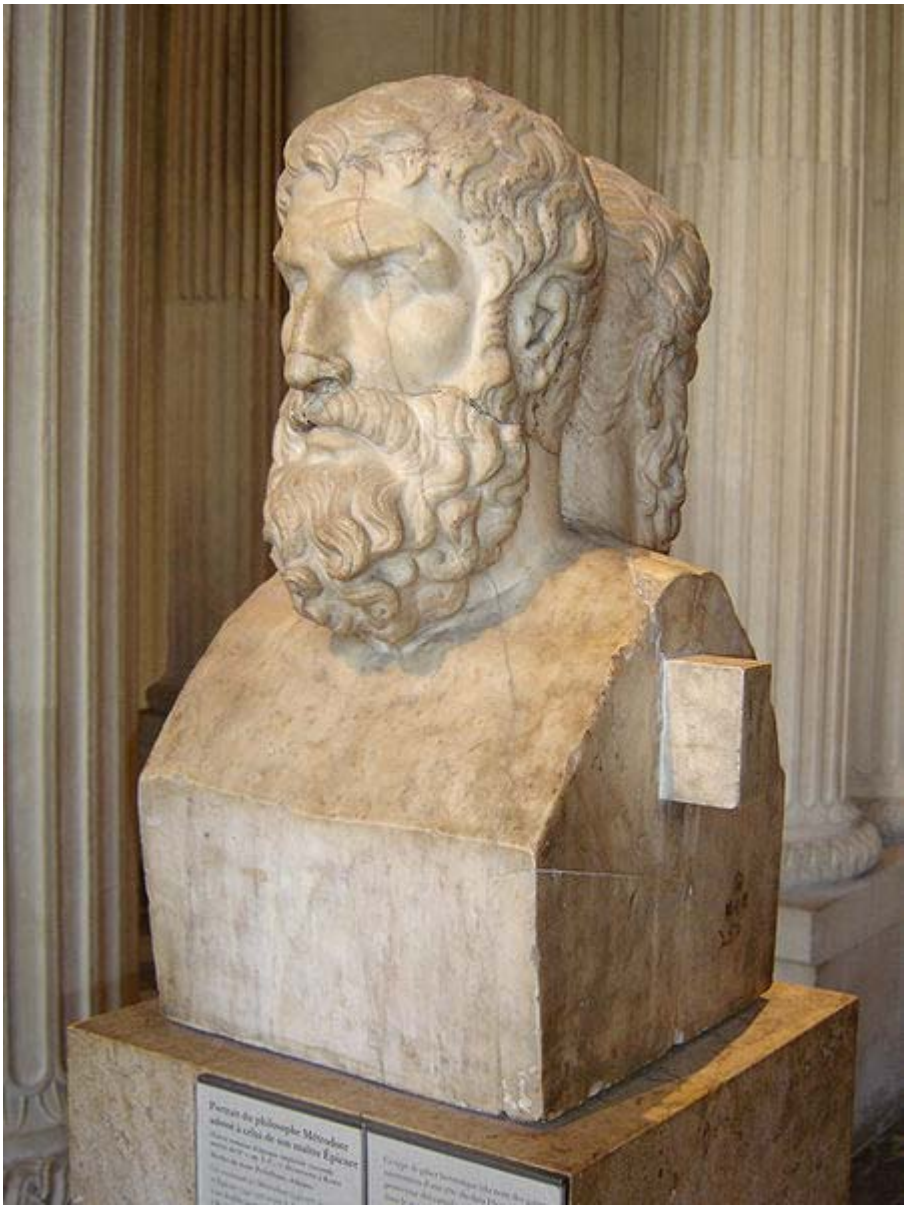
Laboratory, Institute of Biochemistry, University of Cologne

A chemical reaction is a transformation of some substances into one or more other substances. It can be symbolically depicted through a chemical equation. The number of atoms on the left and the right in the equation for a chemical transformation is most often equal. The nature of chemical reactions a substance may undergo and the energy changes that may accompany it are constrained by certain basic rules, known as chemical laws.

Energy and entropy considerations are invariably important in almost all chemical studies. Chemical substances are classified in terms of their structure, phase as well as their chemical compositions. They can be analyzed using the tools of chemical analysis, e.g. spectroscopy and chromatography. Scientists engaged in chemical research are known as chemists. Most chemists specialize in one or more sub-disciplines.

History

Ancient Egyptians pioneered the art of synthetic "wet" chemistry up to 4,000 years ago. By 1000 BC ancient civilizations were using technologies that formed the basis of the various branches of chemistry such as; extracting metal from their ores, making pottery and glazes, fermenting beer and wine, making pigments for cosmetics and painting, extracting chemicals from plants for medicine and perfume, making cheese, dying cloth, tanning leather, rendering fat into soap, making glass, and making alloys like bronze.



Democritus' atomist philosophy was later adopted by Epicurus (341–270 BCE).

The genesis of chemistry can be traced to the widely observed phenomenon of burning that led to metallurgy—the art and science of processing ores to get metals (e.g. metallurgy in ancient India). The greed for gold led to the discovery of the process for its purification, even though the underlying principles were not well understood—it was thought to be a transformation rather than purification. Many scholars in those days thought it reasonable to believe that there exist means for transforming cheaper (base) metals into gold. This gave way to alchemy and the search for the Philosopher's Stone which was believed to bring about such a transformation by mere touch.

Greek atomism dates back to 440 BC, as what might be indicated by the book *De Rerum Natura* (The Nature of Things) written by the Roman Lucretius in 50 BC. Much of the early development of purification methods is described by Pliny the Elder in his *Naturalis Historia*.

A tentative outline is as follows:

1. Egyptian alchemy [3,000 BCE – 400 BCE], formulate early "element" theories such as the Ogdoad.
2. Greek alchemy [332 BCE – 642 CE], the Greek king Alexander the Great conquers Egypt and founds Alexandria, having the world's largest library, where scholars and wise men gather to study.
3. Arab alchemy [642 CE – 1200], the Muslim conquest of Egypt (primarily Alexandria); development of the Scientific Method by Alhazen and Jābir ibn Hayyān revolutionise the field of Chemistry. Jābir (Latin name Geber) accepted many of the ideas of Aristotle but also modified Aristotle's ideas.
4. The House of Wisdom (Arabic: بيت الحكمة; Bait al-Hikma), Al-Andalus (Arabic: الأندلس) and Alexandria (Arabic: ةيردنكسإلا) become the world leading institutions where scientists of all religious and ethnic backgrounds worked together in harmony expanding the reaches of Chemistry in a time known as the Islamic Golden Age.
5. Arabs and Persians continue to dominate the field of Chemistry, mastering it and expanding the boundaries of knowledge and experimentation.
6. European alchemy [1300 – present], Pseudo-Geber builds on Arabic chemistry. From the 12th century, major advances in the chemical arts shifted from Arab lands to western Europe.
7. Chemistry [1661], Boyle writes his classic chemistry text *The Sceptical Chymist*.
8. Chemistry [1787], Lavoisier writes his classic *Elements of Chemistry*.
9. Chemistry [1803], Dalton publishes his *Atomic Theory*.
10. Chemistry [1869], Dmitry Mendeleev presented his Periodic Table being the framework of the modern chemistry

The earliest pioneers of Chemistry, and inventors of the modern scientific method, were medieval Arab and Persian scholars. They introduced precise observation and controlled experimentation into the field and discovered numerous Chemical substances.

"Chemistry as a science was almost created by the Muslims; for in this field, where the Greeks (so far as we know) were confined to industrial experience and vague hypothesis, the Saracens introduced precise observation, controlled experiment, and careful records. They invented and named the alembic (al-anbiq), chemically analyzed innumerable substances, composed lapidaries, distinguished alkalis and acids, investigated their affinities, studied and manufactured hundreds of drugs. Alchemy, which the Muslims inherited from Egypt, contributed to chemistry by a thousand incidental discoveries, and by its method, which was the most scientific of all medieval operations."

The most influential Muslim chemists were Jābir ibn Hayyān (Geber, d. 815), al-Kindi (d. 873), al-Razi (d. 925), al-Biruni (d. 1048) and Alhazen (d. 1039). The works of Jābir became more widely known in Europe through Latin translations by a pseudo-Geber in 14th century Spain, who also wrote some of his own books under the pen name "Geber". The contribution of Indian alchemists and metallurgists in the development of chemistry was also quite significant.

The emergence of chemistry in Europe was primarily due to the recurrent incidence of the plague and blights there during the so called Dark Ages. This gave rise to a need for medicines. It was thought that there exists a universal medicine called the Elixir of Life that can cure all diseases, but like the Philosopher's Stone, it was never found.

Antoine-Laurent de Lavoisier is considered the "Father of Modern Chemistry".

For some practitioners, alchemy was an intellectual pursuit, over time, they got better at it. Paracelsus (1493–1541), for example, rejected the 4-elemental theory and with only a vague understanding of his chemicals and medicines, formed a hybrid of alchemy and science in what was to be called *iatrochemistry*. Similarly, the influences of philosophers such as Sir Francis Bacon (1561–1626) and René Descartes (1596–1650), who demanded more rigor in mathematics and in removing bias from scientific observations, led to a scientific revolution. In chemistry, this began with Robert Boyle (1627–1691), who came up with an equation known as Boyle's Law about the characteristics of gaseous state.

Chemistry indeed came of age when Antoine Lavoisier (1743–1794), developed the theory of Conservation of mass in 1783; and the development of the Atomic Theory by John Dalton around 1800. The Law of Conservation of Mass resulted in the reformulation of chemistry based on this law and the oxygen theory of combustion, which was largely based on the work of Lavoisier. Lavoisier's fundamental contributions to chemistry were a result of a conscious effort to fit all experiments into the framework of a single theory. He established the consistent use of the chemical balance, used oxygen to overthrow the phlogiston theory, and developed a new system of chemical nomenclature and made contribution to the modern metric system. Lavoisier also worked to translate the archaic and technical language of chemistry into something that could be easily understood by the largely uneducated masses, leading to an increased public interest in chemistry. All these advances in chemistry led to what is usually called the chemical revolution. The contributions of Lavoisier led to what is now called modern chemistry—the chemistry that is studied in educational institutions all over the world. It is because of these and other contributions that Antoine Lavoisier is often celebrated as the "Father of Modern Chemistry". The later discovery of Friedrich Wöhler that many natural substances, organic compounds, can indeed be synthesized in a chemistry laboratory also helped the modern chemistry to mature from its infancy.

The discovery of the chemical elements has a long history from the days of alchemy and culminating in the discovery of the periodic table of the chemical elements by Dmitri Mendeleev (1834–1907) and later discoveries of some synthetic elements.

Etymology

The word *chemistry* comes from the earlier study of alchemy, which is a set of practices that encompasses elements of chemistry, metallurgy, philosophy, astrology, astronomy, mysticism and medicine. Alchemy in turn is derived from the Arabic word "ءايميك" meaning "value"; it is commonly thought of as the quest to turn lead or another common starting material into gold. This linguistic relation between the pursuit of value and alchemy is thought to have Egyptian origins. Many believe that the Arabic word "alchemy" is derived from the word **Chemi** or **Kimi**, which is the ancient name of Egypt in Egyptian. The word was subsequently borrowed by the Greeks, and from the Greeks by the Arabs when they occupied Alexandria (Egypt) in the 7th century. The Arabs added the Arabic definite article "al" to the word, resulting in the word "ءايميكلا" (al-kīmiyā). Thus, an alchemist was called a 'chemist' in popular speech, and later the suffix "-ry" was added to this to describe the art of the chemist as "chemistry".

Definitions

In retrospect, the definition of chemistry has changed over time, as new discoveries and theories add to the functionality of the science. Shown below are some of the standard definitions used by various noted chemists:

- **Alchemy** (330) – the study of the composition of waters, movement, growth, embodying, disembodying, drawing the spirits from bodies and bonding the spirits within bodies (Zosimos).
- **Chymistry** (1661) – the subject of the material principles of mixt bodies (Boyle).
- **Chymistry** (1663) – a scientific art, by which one learns to dissolve bodies, and draw from them the different substances on their composition, and how to unite them again, and exalt them to a higher perfection (Glaser).
- **Chemistry** (1730) – the art of resolving mixt, compound, or aggregate bodies into their principles; and of composing such bodies from those principles (Stahl).
- **Chemistry** (1837) – the science concerned with the laws and effects of molecular forces (Dumas).
- **Chemistry** (1947) – the science of substances: their structure, their properties, and the reactions that change them into other substances (Pauling).
- **Chemistry** (1998) – the study of matter and the changes it undergoes (Chang).

Basic concepts

Several concepts are essential for the study of chemistry; some of them are:

Atom

An *atom* is the basic unit of chemistry. It consists of a positively charged core (the atomic nucleus) which contains protons and neutrons, and which maintains a number of electrons to balance the positive charge in the nucleus. The atom is also the smallest

entity that can be envisaged to retain some of the chemical properties of the element, such as electronegativity, ionization potential, preferred oxidation state(s), coordination number, and preferred types of bonds to form (e.g., metallic, ionic, covalent).

Element

The concept of *chemical element* is related to that of chemical substance. A chemical element is specifically a substance which is composed of a single type of atom. A chemical element is characterized by a particular number of protons in the nuclei of its atoms. This number is known as the atomic number of the element. For example, all atoms with 6 protons in their nuclei are atoms of the chemical element carbon, and all atoms with 92 protons in their nuclei are atoms of the element uranium. Ninety–four different chemical elements or types of atoms based on the number of protons exist naturally. A further 18 have been recognised by IUPAC as existing artificially only. Although all the nuclei of all atoms belonging to one element will have the same number of protons, they may not necessarily have the same number of neutrons; such atoms are termed isotopes. In fact several isotopes of an element may exist.

The most convenient presentation of the chemical elements is in the periodic table of the chemical elements, which groups elements by atomic number. Due to its ingenious arrangement, groups, or columns, and periods, or rows, of elements in the table either share several chemical properties, or follow a certain trend in characteristics such as atomic radius, electronegativity, etc. Lists of the elements by name, by symbol, and by atomic number are also available.

Compound

A *compound* is a substance with a *particular ratio* of atoms of particular chemical elements which determines its composition, and a particular organization which determines chemical properties. For example, water is a compound containing hydrogen and oxygen in the ratio of two to one, with the oxygen atom between the two hydrogen atoms, and an angle of 104.5° between them. Compounds are formed and interconverted by chemical reactions.

Substance

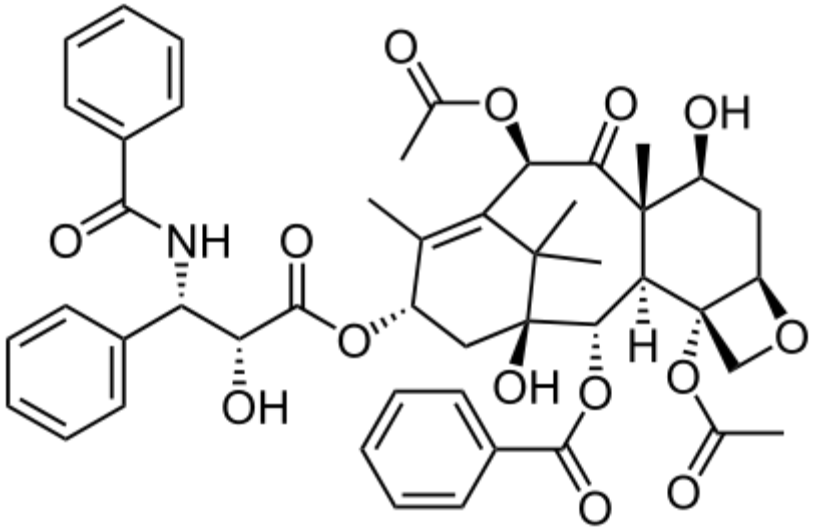
A chemical substance is a kind of matter with a definite composition and set of properties. Strictly speaking, a mixture of compounds, elements or compounds and elements is not a chemical substance, but it may be called a chemical. Most of the substances we encounter in our daily life are some kind of mixture; for example: air, alloys, biomass, etc.

Nomenclature of substances is a critical part of the language of chemistry. Generally it refers to a system for naming chemical compounds. Earlier in the history of chemistry substances were given name by their discoverer, which often led to some confusion and difficulty. However, today the IUPAC system of chemical nomenclature allows chemists to specify by name specific compounds amongst the vast variety of possible chemicals. The standard nomenclature of chemical substances is set by the International Union of Pure and Applied Chemistry (IUPAC). There are well-defined systems in place for naming chemical species. Organic compounds are named according to the organic

nomenclature system. Inorganic compounds are named according to the inorganic nomenclature system. In addition the Chemical Abstracts Service has devised a method to index chemical substance. In this scheme each chemical substance is identifiable by a number known as CAS registry number.

Molecule

A *molecule* is the smallest indivisible portion of a pure chemical substance that has its unique set of chemical properties, that is, its potential to undergo a certain set of chemical reactions with other substances. Molecules can exist as electrically neutral units unlike ions. Molecules are typically a set of atoms bound together by covalent bonds, such that the structure is electrically neutral and all valence electrons are paired with other electrons either in bonds or in lone pairs.



A molecular structure depicts the bonds and relative positions of atoms in a molecule such as that in Paclitaxel shown here

Not all substances consist of discrete molecules. Most chemical elements are composed of lone atoms as their smallest discrete unit. Other types of substances, such as ionic compounds and network solids, are organized in such a way as to lack the existence of identifiable molecules *per se*. Instead, these substances are discussed in terms of formula units or unit cells as the smallest repeating structure within the substance; as they lack identifiable molecules.

One of the main characteristic of a molecule is its geometry often called its structure. While the structure of diatomic, triatomic or tetra atomic molecules may be trivial, (linear, angular pyramidal etc.) the structure of polyatomic molecules, that are constituted of more than six atoms (of several elements) can be crucial for its chemical nature.

Mole and amount of substance

Mole is a unit to measure amount of substance (also called chemical amount). A mole is the amount of a substance that contains as many elementary entities (atoms, molecules or

ions) as there are atoms in 0.012 kilogram (or 12 grams) of carbon-12, where the carbon-12 atoms are unbound, at rest and in their ground state. The number of entities per mole is known as the Avogadro constant, and is determined empirically. The currently accepted value is $6.02214179(30)\times10^{23}$ mol^{-1} (2007 CODATA). One way to understand the meaning of the term "mole" is to compare and contrast it to terms such as dozen. Just as one dozen eggs contains 12 individual eggs, one mole contains $6.02214179(30)\times10^{23}$ atoms, molecules or other particles. The term is used because it is much easier to say, for example, 1 mole of carbon, than it is to say $6.02214179(30)\times10^{23}$ carbon atoms, and because moles of chemicals represent a scale that is easy to experience.

The amount of substance of a solute per volume of solution is known as amount of substance concentration, or molarity for short. Molarity is the quantity most commonly used to express the concentration of a solution in the chemical laboratory. The most commonly used units for molarity are mol/L (the official SI units are mol/m^3).

Ions and salts

An *ion* is a charged species, an atom or a molecule, that has lost or gained one or more electrons. Positively charged cations (e.g. sodium cation Na^+) and negatively charged anions (e.g. chloride Cl^-) can form a crystalline lattice of neutral salts (e.g. sodium chloride NaCl). Examples of polyatomic ions that do not split up during acid-base reactions are hydroxide (OH^-) and phosphate (PO_4^{3-}).

Ions in the gaseous phase are often known as plasma.

Acidity and basicity

A substance can often be classified as an acid or a base. There are several different theories which explain acid-base behavior. The simplest is Arrhenius theory, which states than an acid is a substance that produces hydronium ions when it is dissolved in water, and a base is one that produces hydroxide ions when dissolved in water. According to Brønsted–Lowry acid-base theory, acids are substances that donate a positive hydrogen ion to another substance in a chemical reaction; by extension, a base is the substance which receives that hydrogen ion. A third common theory is Lewis acid-base theory, which is based on the formation of new chemical bonds. Lewis theory explains that an acid is a substance which is capable of accepting a pair of electrons from another substance during the process of bond formation, while a base is a substance which can provide a pair of electrons to form a new bond. According to concept as per Lewis, the crucial things being exchanged are charges. There are several other ways in which a substance may be classified as an acid or a base, as is evident in the history of this concept

Acid strength is commonly measured by two methods. One measurement, based on the Arrhenius definition of acidity, is pH, which is a measurement of the hydronium ion concentration in a solution, as expressed on a negative logarithmic scale. Thus, solutions that have a low pH have a high hydronium ion concentration, and can be said to be more acidic. The other measurement, based on the Brønsted–Lowry definition, is the acid dissociation constant (K_a), which measure the relative ability of a substance to act as an acid under the Brønsted–Lowry definition of an acid. That is, substances with a higher K_a

are more likely to donate hydrogen ions in chemical reactions than those with lower K_a values.

Phase

In addition to the specific chemical properties that distinguish different chemical classifications chemicals can exist in several phases. For the most part, the chemical classifications are independent of these bulk phase classifications; however, some more exotic phases are incompatible with certain chemical properties. A *phase* is a set of states of a chemical system that have similar bulk structural properties, over a range of conditions, such as pressure or temperature. Physical properties, such as density and refractive index tend to fall within values characteristic of the phase. The phase of matter is defined by the *phase transition*, which is when energy put into or taken out of the system goes into rearranging the structure of the system, instead of changing the bulk conditions.

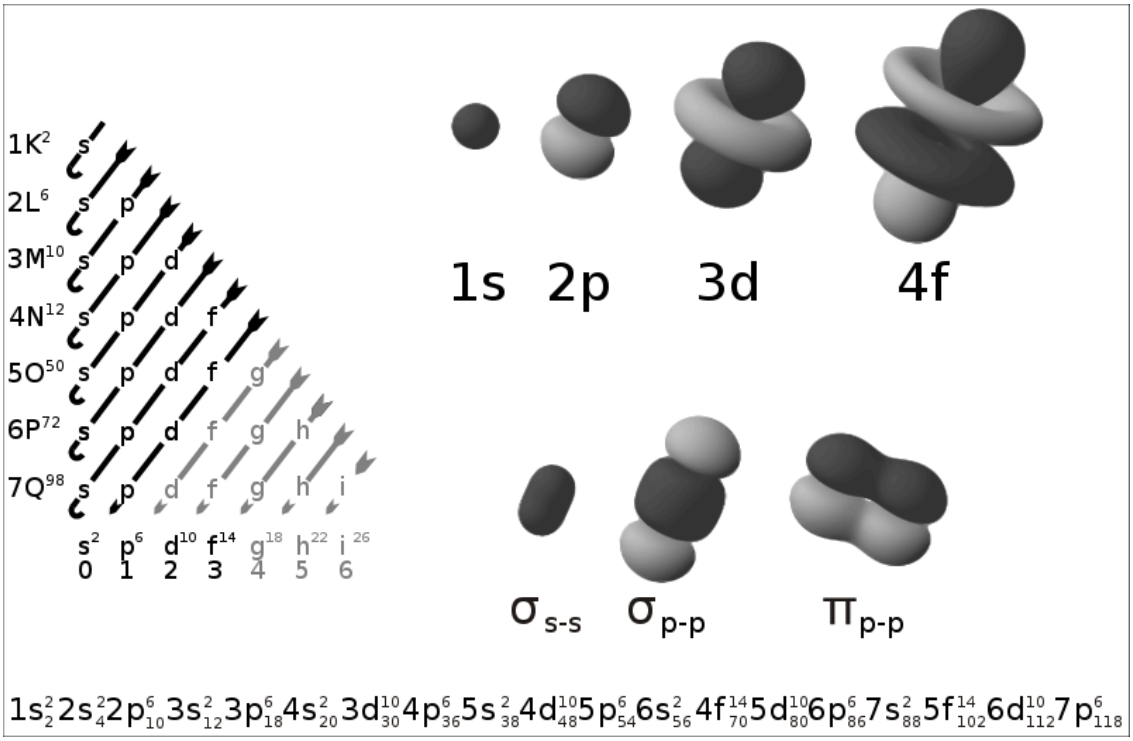
Sometimes the distinction between phases can be continuous instead of having a discrete boundary, in this case the matter is considered to be in a supercritical state. When three states meet based on the conditions, it is known as a triple point and since this is invariant, it is a convenient way to define a set of conditions.

The most familiar examples of phases are solids, liquids, and gases. Many substances exhibit multiple solid phases. For example, there are three phases of solid iron (alpha, gamma, and delta) that vary based on temperature and pressure. A principal difference between solid phases is the crystal structure, or arrangement, of the atoms. Another phase commonly encountered in the study of chemistry is the *aqueous* phase, which is the state of substances dissolved in aqueous solution (that is, in water). Less familiar phases include plasmas, Bose-Einstein condensates and fermionic condensates and the paramagnetic and ferromagnetic phases of magnetic materials. While most familiar phases deal with three-dimensional systems, it is also possible to define analogs in two-dimensional systems, which has received attention for its relevance to systems in biology.

Redox

It is a concept related to the ability of atoms of various substances to lose or gain electrons. Substances that have the ability to oxidize other substances are said to be oxidative and are known as oxidizing agents, oxidants or oxidizers. An oxidant removes electrons from another substance. Similarly, substances that have the ability to reduce other substances are said to be reductive and are known as reducing agents, reductants, or reducers. A reductant transfers electrons to another substance, and is thus oxidized itself. And because it "donates" electrons it is also called an electron donor. Oxidation and reduction properly refer to a change in oxidation number—the actual transfer of electrons may never occur. Thus, oxidation is better defined as an increase in oxidation number, and reduction as a decrease in oxidation number.

Bonding



Electron atomic and molecular orbitals

Atoms sticking together in molecules or crystals are said to be bonded with one another. A chemical bond may be visualized as the multipole balance between the positive charges in the nuclei and the negative charges oscillating about them. More than simple attraction and repulsion, the energies and distributions characterize the availability of an electron to bond to another atom.

A chemical bond can be a covalent bond, an ionic bond, a hydrogen bond or just because of Van der Waals force. Each of these kind of bond is ascribed to some potential. These potentials create the interactions which hold atoms together in molecules or crystals. In many simple compounds, Valence Bond Theory, the Valence Shell Electron Pair Repulsion model (VSEPR), and the concept of oxidation number can be used to explain molecular structure and composition. Similarly, theories from classical physics can be used to predict many ionic structures. With more complicated compounds, such as metal complexes, valence bond theory is less applicable and alternative approaches, such as the molecular orbital theory, are generally used.

Reaction

When a chemical substance is transformed as a result of its interaction with another or energy, a chemical reaction is said to have occurred. *Chemical reaction* is therefore a concept related to the 'reaction' of a substance when it comes in close contact with another, whether as a mixture or a solution; exposure to some form of energy, or both. It results in some energy exchange between the constituents of the reaction as well with the system environment which may be a designed vessels which are often laboratory glassware. Chemical reactions can result in the formation or dissociation of molecules,

that is, molecules breaking apart to form two or more smaller molecules, or rearrangement of atoms within or across molecules. Chemical reactions usually involve the making or breaking of chemical bonds. Oxidation, reduction, dissociation, acid-base neutralization and molecular rearrangement are some of the commonly used kinds of chemical reactions.

A chemical reaction can be symbolically depicted through a chemical equation. While in a non-nuclear chemical reaction the number and kind of atoms on both sides of the equation are equal, for a nuclear reaction this holds true only for the nuclear particles viz. protons and neutrons.

The sequence of steps in which the reorganization of chemical bonds may be taking place in the course of a chemical reaction is called its mechanism. A chemical reaction can be envisioned to take place in a number of steps, each of which may have a different speed. Many reaction intermediates with variable stability can thus be envisaged during the course of a reaction. Reaction mechanisms are proposed to explain the kinetics and the relative product mix of a reaction. Many physical chemists specialize in exploring and proposing the mechanisms of various chemical reactions. Several empirical rules, like the Woodward-Hoffmann rules often come handy while proposing a mechanism for a chemical reaction.

According to the IUPAC gold book a chemical reaction is a process that results in the interconversion of chemical species". Accordingly, a chemical reaction may be an elementary reaction or a stepwise reaction. An additional caveat is made, in that this definition includes cases where the interconversion of conformers is experimentally observable. Such detectable chemical reactions normally involve sets of molecular entities as indicated by this definition, but it is often conceptually convenient to use the term also for changes involving single molecular entities (i.e. 'microscopic chemical events').

Equilibrium

Although the concept of equilibrium is widely used across sciences, in the context of chemistry, it arises whenever a number of different states of the chemical composition are possible. For example, in a mixture of several chemical compounds that can react with one another, or when a substance can be present in more than one kind of phase. A system of chemical substances at equilibrium even though having an unchanging composition is most often not static; molecules of the substances continue to react with one another thus giving rise to a dynamic equilibrium. Thus the concept describes the state in which the parameters such as chemical composition remain unchanged over time. Chemicals present in biological systems are invariably not at equilibrium; rather they are far from equilibrium.

Energy

In the context of chemistry, energy is an attribute of a substance as a consequence of its atomic, molecular or aggregate structure. Since a chemical transformation is accompanied by a change in one or more of these kinds of structure, it is invariably accompanied by an increase or decrease of energy of the substances involved. Some energy is transferred between the surroundings and the reactants of the reaction in the

form of heat or light; thus the products of a reaction may have more or less energy than the reactants. A reaction is said to be exergonic if the final state is lower on the energy scale than the initial state; in the case of endergonic reactions the situation is the reverse. A reaction is said to be exothermic if the reaction releases heat to the surroundings; in the case of endothermic reactions, the reaction absorbs heat from the surroundings.

Chemical reactions are invariably not possible unless the reactants surmount an energy barrier known as the activation energy. The *speed* of a chemical reaction (at given temperature T) is related to the activation energy E, by the Boltzmann's population factor $e^{-E/kT}$ - that is the probability of molecule to have energy greater than or equal to E at the given temperature T. This exponential dependence of a reaction rate on temperature is known as the Arrhenius equation. The activation energy necessary for a chemical reaction can be in the form of heat, light, electricity or mechanical force in the form of ultrasound.

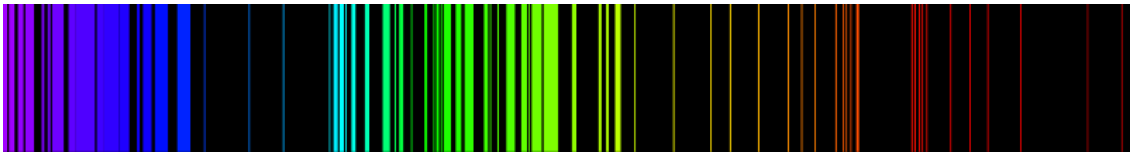
A related concept free energy, which also incorporates entropy considerations, is a very useful means for predicting the feasibility of a reaction and determining the state of equilibrium of a chemical reaction, in chemical thermodynamics. A reaction is feasible only if the total change in the Gibbs free energy is negative, $\Delta G \leq 0$; if it is equal to zero the chemical reaction is said to be at equilibrium.

There exist only limited possible states of energy for electrons, atoms and molecules. These are determined by the rules of quantum mechanics, which require quantization of energy of a bound system. The atoms/molecules in a higher energy state are said to be excited. The molecules/atoms of substance in an excited energy state are often much more reactive; that is, more amenable to chemical reactions.

The phase of a substance is invariably determined by its energy and the energy of its surroundings. When the intermolecular forces of a substance are such that the energy of the surroundings is not sufficient to overcome them, it occurs in a more ordered phase like liquid or solid as is the case with water (H_2O); a liquid at room temperature because its molecules are bound by hydrogen bonds. Whereas hydrogen sulfide (H_2S) is a gas at room temperature and standard pressure, as its molecules are bound by weaker dipole-dipole interactions.

The transfer of energy from one chemical substance to another depends on the *size* of energy quanta emitted from one substance. However, heat energy is often transferred more easily from almost any substance to another because the phonons responsible for vibrational and rotational energy levels in a substance have much less energy than photons invoked for the electronic energy transfer. Thus, because vibrational and rotational energy levels are more closely spaced than electronic energy levels, heat is more easily transferred between substances relative to light or other forms of electronic energy. For example, ultraviolet electromagnetic radiation is not transferred with as much efficacy from one substance to another as thermal or electrical energy.

The existence of characteristic energy levels for different chemical substances is useful for their identification by the analysis of spectral lines. Different kinds of spectra are often used in chemical spectroscopy, e.g. IR, microwave, NMR, ESR, etc. Spectroscopy is also used to identify the composition of remote objects - like stars and distant galaxies - by analyzing their radiation spectra.



Emission spectrum of iron

The term chemical energy is often used to indicate the potential of a chemical substance to undergo a transformation through a chemical reaction or to transform other chemical substances.

Chemical laws

Chemical reactions are governed by certain laws, which have become fundamental concepts in chemistry. Some of them are:

- Avogadro's law
- Beer-Lambert law
- Boyle's law (1662, relating pressure and volume)
- Charles's law (1787, relating volume and temperature)
- Fick's law of diffusion
- Gay-Lussac's law (1809, relating pressure and temperature)
- Henry's law
- Hess's Law
- Law of conservation of energy leads to the important concepts of equilibrium, thermodynamics, and kinetics.
- Law of conservation of mass, according to the modern physics it is actually energy that is conserved, and that energy and mass are related; a concept which becomes important in nuclear chemistry.
- Law of definite composition, although in many systems (notably biomacromolecules and minerals) the ratios tend to require large numbers, and are frequently represented as a fraction.
- Law of multiple proportions
- Raoult's Law

Subdisciplines

Chemistry is typically divided into several major sub-disciplines. There are also several main cross-disciplinary and more specialized fields of chemistry.

- Analytical chemistry is the analysis of material samples to gain an understanding of their chemical composition and structure. Analytical chemistry incorporates standardized experimental methods in chemistry. These methods may be used in all subdisciplines of chemistry, excluding purely theoretical chemistry.

- Biochemistry is the study of the chemicals, chemical reactions and chemical interactions that take place in living organisms. Biochemistry and organic chemistry are closely related, as in medicinal chemistry or neurochemistry. Biochemistry is also associated with molecular biology and genetics.

- Inorganic chemistry is the study of the properties and reactions of inorganic compounds. The distinction between organic and inorganic disciplines is not absolute and there is much overlap, most importantly in the sub-discipline of organometallic chemistry.

- Materials chemistry is the preparation, characterization, and understanding of substances with a useful function. The field is a new breadth of study in graduate programs, and it integrates elements from all classical areas of chemistry with a focus on fundamental issues that are unique to materials. Primary systems of study include the chemistry of condensed phases (solids, liquids, polymers) and interfaces between different phases.

- Neurochemistry is the study of neurochemicals; including transmitters, peptides, proteins, lipids, sugars, and nucleic acids; their interactions, and the roles they play in forming, maintaining, and modifying the nervous system.

- Nuclear chemistry is the study of how subatomic particles come together and make nuclei. Modern Transmutation is a large component of nuclear chemistry, and the table of nuclides is an important result and tool for this field.

- Organic chemistry is the study of the structure, properties, composition, mechanisms, and reactions of organic compounds. An organic compound is defined as any compound based on a carbon skeleton.

- Physical chemistry is the study of the physical and fundamental basis of chemical systems and processes. In particular, the energetics and dynamics of such systems and processes are of interest to physical chemists. Important areas of study include chemical thermodynamics, chemical kinetics, electrochemistry, statistical mechanics, spectroscopy, and more recently, astrochemistry. Physical chemistry has large overlap with molecular physics. Physical chemistry involves the use of infinitesimal calculus in deriving equations. It is usually associated with quantum chemistry and theoretical chemistry. Physical chemistry is a distinct discipline from chemical physics, but again, there is very strong overlap.

- Theoretical chemistry is the study of chemistry via fundamental theoretical reasoning (usually within mathematics or physics). In particular the application of quantum mechanics to chemistry is called quantum chemistry. Since the end of the Second World War, the development of computers has allowed a systematic development of computational chemistry, which is the art of developing and applying computer programs for solving chemical problems. Theoretical chemistry has large overlap with (theoretical and experimental) condensed matter physics and molecular physics.

Other fields include agrochemistry, astrochemistry (and cosmochemistry), atmospheric chemistry, chemical engineering, chemical biology, chemo-informatics, electrochemistry, environmental chemistry, femtochemistry, flavor chemistry, flow chemistry, geochemistry, green chemistry, histochemistry, history of chemistry, hydrogenation chemistry, immunochemistry, marine chemistry, materials science, mathematical chemistry, mechanochemistry, medicinal chemistry, molecular biology, molecular mechanics, nanotechnology, natural product chemistry, oenology, organometallic

chemistry, petrochemistry, pharmacology, photochemistry, physical organic chemistry, phytochemistry, polymer chemistry, radiochemistry, solid-state chemistry, sonochemistry, supramolecular chemistry, surface chemistry, synthetic chemistry, thermochemistry, and many others.

Chemical industry

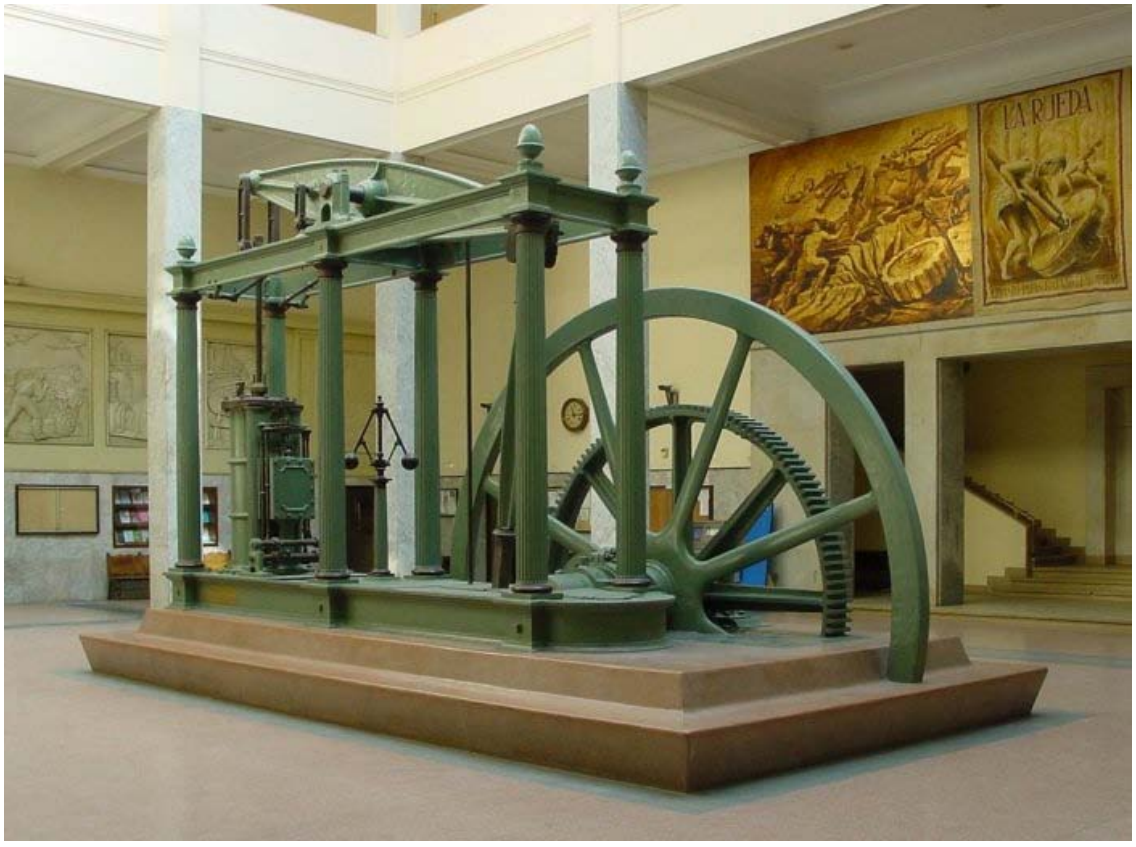
The chemical industry represents an important economic activity. The global top 50 chemical producers in 2004 had sales of 587 billion US dollars with a profit margin of 8.1% and research and development spending of 2.1% of total chemical sales.

Professional societies

- American Chemical Society
- American Society for Neurochemistry
- Chemical Institute of Canada
- Chemical Society of Peru
- International Union of Pure and Applied Chemistry
- Royal Australian Chemical Institute
- Royal Netherlands Chemical Society
- Royal Society of Chemistry
- Society of Chemical Industry
- World Association of Theoretical and Computational Chemists
- Others

Chapter 3

Engineering



The Watt steam engine, a major driver in the Industrial Revolution, underscores the importance of engineering in modern history. This model is on display at the main building of the ETSIIM in Madrid, Spain

Engineering is the discipline, art, and profession of acquiring and applying scientific, mathematical, economic, social, and practical knowledge to design and build structures, machines, devices, systems, materials and processes that safely realize improvements to the lives of people.

The American Engineers' Council for Professional Development (ECPD, the predecessor of ABET) has defined "engineering" as:

[T]he creative application of scientific principles to design or develop structures, machines, apparatus, or manufacturing processes, or works utilizing them singly or in combination; or to construct or operate the same with full cognizance of their design; or to forecast their behavior under specific operating conditions; all as respects an intended function, economics of operation and safety to life and property.

One who practices engineering is called an engineer, and those licensed to do so may have more formal designations such as Professional Engineer, Chartered Engineer, Incorporated Engineer, Ingenieur or European Engineer. The broad discipline of engineering encompasses a range of more specialized subdisciplines, each with a more specific emphasis on certain fields of application and particular areas of technology.

History

The *concept* of engineering has existed since ancient times as humans devised fundamental inventions such as the pulley, lever, and wheel. Each of these inventions is consistent with the modern definition of engineering, exploiting basic mechanical principles to develop useful tools and objects.

The term *engineering* itself has a much more recent etymology, deriving from the word *engineer*, which itself dates back to 1325, when an *engine'er* (literally, one who operates an *engine*) originally referred to "a constructor of military engines." In this context, now obsolete, an "engine" referred to a military machine, *i.e.*, a mechanical contraption used in war (for example, a catapult). Notable exceptions of the obsolete usage which have survived to the present day are military engineering corps, *e.g.*, the U.S. Army Corps of Engineers.

The word "engine" itself is of even older origin, ultimately deriving from the Latin *ingenium* (c. 1250), meaning "innate quality, especially mental power, hence a clever invention."

Later, as the design of civilian structures such as bridges and buildings matured as a technical discipline, the term civil engineering entered the lexicon as a way to distinguish between those specializing in the construction of such non-military projects and those involved in the older discipline of military engineering.

Ancient era

The Pharos of Alexandria, the pyramids in Egypt, the Hanging Gardens of Babylon, the Acropolis and the Parthenon in Greece, the Roman aqueducts, Via Appia and the Colosseum, Teotihuacán and the cities and pyramids of the Mayan, Inca and Aztec Empires, the Great Wall of China, among many others, stand as a testament to the ingenuity and skill of the ancient civil and military engineers.

The earliest civil engineer known by name is Imhotep. As one of the officials of the Pharaoh, Djosèr, he probably designed and supervised the construction of the Pyramid of

Djoser (the Step Pyramid) at Saqqara in Egypt around 2630-2611 BC. He may also have been responsible for the first known use of columns in architecture.

Ancient Greece developed machines in both the civilian and military domains. The Antikythera mechanism, the first known mechanical computer, and the mechanical inventions of Archimedes are examples of early mechanical engineering. Some of Archimedes' inventions as well as the Antikythera mechanism required sophisticated knowledge of differential gearing or epicyclic gearing, two key principles in machine theory that helped design the gear trains of the Industrial revolution, and are still widely used today in diverse fields such as robotics and automotive engineering.

Chinese, Greek and Roman armies employed complex military machines and inventions such as artillery which was developed by the Greeks around the 4th century B.C., the trireme, the ballista and the catapult. In the Middle Ages, the Trebuchet was developed.

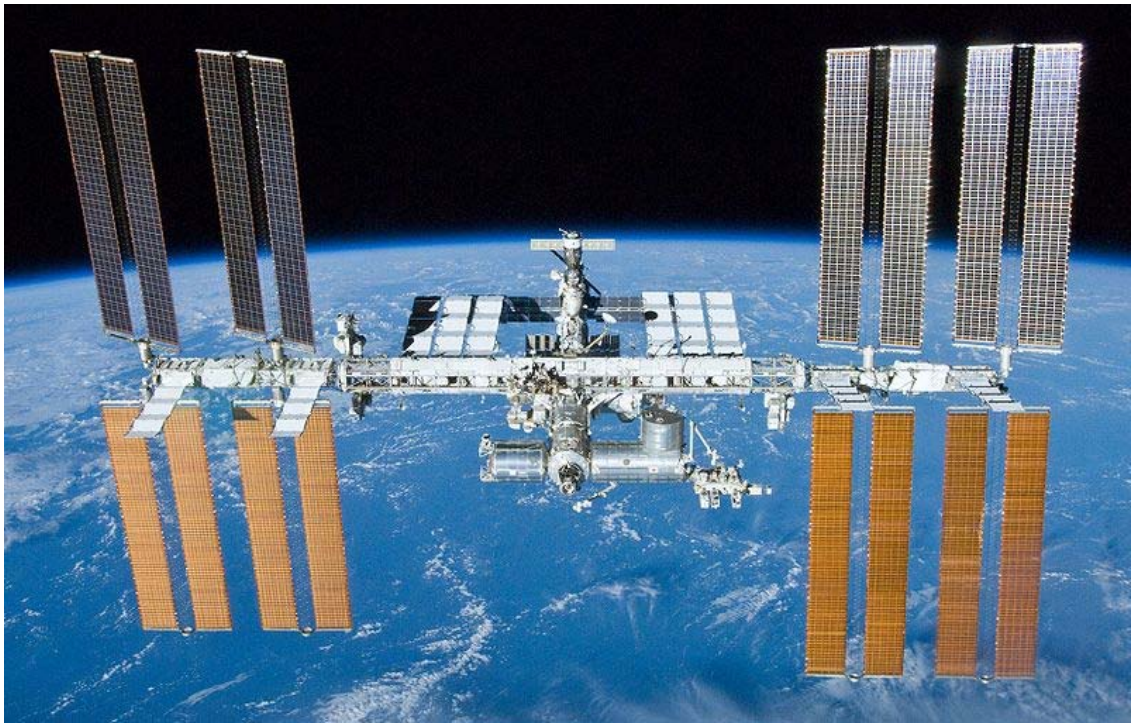
Renaissance era

The first electrical engineer is considered to be William Gilbert, with his 1600 publication of De Magnete, who was the originator of the term "electricity".

The first steam engine was built in 1698 by mechanical engineer Thomas Savery. The development of this device gave rise to the industrial revolution in the coming decades, allowing for the beginnings of mass production.

With the rise of engineering as a profession in the eighteenth century, the term became more narrowly applied to fields in which mathematics and science were applied to these ends. Similarly, in addition to military and civil engineering the fields then known as the mechanic arts became incorporated into engineering.

Modern era



The International Space Station represents a modern engineering challenge from many disciplines.

Electrical engineering can trace its origins in the experiments of Alessandro Volta in the 1800s, the experiments of Michael Faraday, Georg Ohm and others and the invention of the electric motor in 1872. The work of James Maxwell and Heinrich Hertz in the late 19th century gave rise to the field of Electronics. The later inventions of the vacuum tube and the transistor further accelerated the development of electronics to such an extent that electrical and electronics engineers currently outnumber their colleagues of any other Engineering specialty.

The inventions of Thomas Savery and the Scottish engineer James Watt gave rise to modern Mechanical Engineering. The development of specialized machines and their maintenance tools during the industrial revolution led to the rapid growth of Mechanical Engineering both in its birthplace Britain and abroad.

Chemical Engineering, like its counterpart Mechanical Engineering, developed in the nineteenth century during the Industrial Revolution. Industrial scale manufacturing demanded new materials and new processes and by 1880 the need for large scale production of chemicals was such that a new industry was created, dedicated to the development and large scale manufacturing of chemicals in new industrial plants. The role of the chemical engineer was the design of these chemical plants and processes.

Aeronautical Engineering deals with aircraft design while Aerospace Engineering is a more modern term that expands the reach envelope of the discipline by including spacecraft design. Its origins can be traced back to the aviation pioneers around the turn of the century from the 19th century to the 20th although the work of Sir George Cayley has recently been dated as being from the last decade of the 18th century. Early

knowledge of aeronautical engineering was largely empirical with some concepts and skills imported from other branches of engineering.

The first PhD in engineering (technically, *applied science and engineering*) awarded in the United States went to Willard Gibbs at Yale University in 1863; it was also the second PhD awarded in science in the U.S.

Only a decade after the successful flights by the Wright brothers, the 1920s saw extensive development of aeronautical engineering through development of World War I military aircraft. Meanwhile, research to provide fundamental background science continued by combining theoretical physics with experiments.

In 1990, with the rise of computer technology, the first search engine was built by computer engineer Alan Emtage.

Main branches of engineering

Engineering, much like other science, is a broad discipline which is often broken down into several sub-disciplines. These disciplines concern themselves with differing areas of engineering work. Although initially an engineer will usually be trained in a specific discipline, throughout an engineer's career the engineer may become multi-disciplined, having worked in several of the outlined areas. Engineering is often characterized as having four main branches:

- Chemical engineering – The exploitation of chemical principles in order to carry out large scale chemical process, as well as designing new specialty materials and fuels.
- Civil engineering – The design and construction of public and private works, such as infrastructure (roads, railways, water supply and treatment etc.), bridges and buildings.
- Electrical engineering – a very broad area that may encompass the design and study of various electrical & electronic systems, such as electrical circuits, generators, motors, electromagnetic/electromechanical devices, electronic devices, electronic circuits, optical fibers, optoelectronic devices, computer systems, telecommunications and electronics.
- Mechanical engineering – The design of physical or mechanical systems, such as power and energy systems, aerospace/aircraft products, weapon systems, transportation products engines, compressors, powertrains, kinematic chains, vacuum technology, and vibration isolation equipment.

Beyond these four, sources vary on other main branches. Historically, naval engineering and mining engineering were major branches. Modern fields sometimes included as major branches include aerospace, architectural, biomedical industrial, and nuclear engineering.

New specialties sometimes combine with the traditional fields and form new branches. A new or emerging area of application will commonly be defined temporarily as a permutation or subset of existing disciplines; there is often gray area as to when a given sub-field becomes large and/or prominent enough to warrant classification as a new

"branch." One key indicator of such emergence is when major universities start establishing departments and programs in the new field.

For each of these fields there exists considerable overlap, especially in the areas of the application of sciences to their disciplines such as physics, chemistry and mathematics.

Methodology

Design of a turbine requires collaboration of engineers from many fields, as the system is subject to mechanical, electro-magnetic and chemical processes. The blades, rotor and stator as well as the steam cycle all need to be carefully designed and optimised.

Engineers apply the sciences of physics and mathematics to find suitable solutions to problems or to make improvements to the status quo. More than ever, engineers are now required to have knowledge of relevant sciences for their design projects, as a result, they keep on learning new material throughout their career.

If multiple options exist, engineers weigh different design choices on their merits and choose the solution that best matches the requirements. The crucial and unique task of the engineer is to identify, understand, and interpret the constraints on a design in order to produce a successful result. It is usually not enough to build a technically successful product; it must also meet further requirements.

Constraints may include available resources, physical, imaginative or technical limitations, flexibility for future modifications and additions, and other factors, such as requirements for cost, safety, marketability, productibility, and serviceability. By understanding the constraints, engineers derive specifications for the limits within which a viable object or system may be produced and operated.

Problem solving

Engineers use their knowledge of science, mathematics, logic, economics, and appropriate experience or tacit knowledge to find suitable solutions to a problem. Creating an appropriate mathematical model of a problem allows them to analyze it (sometimes definitively), and to test potential solutions.

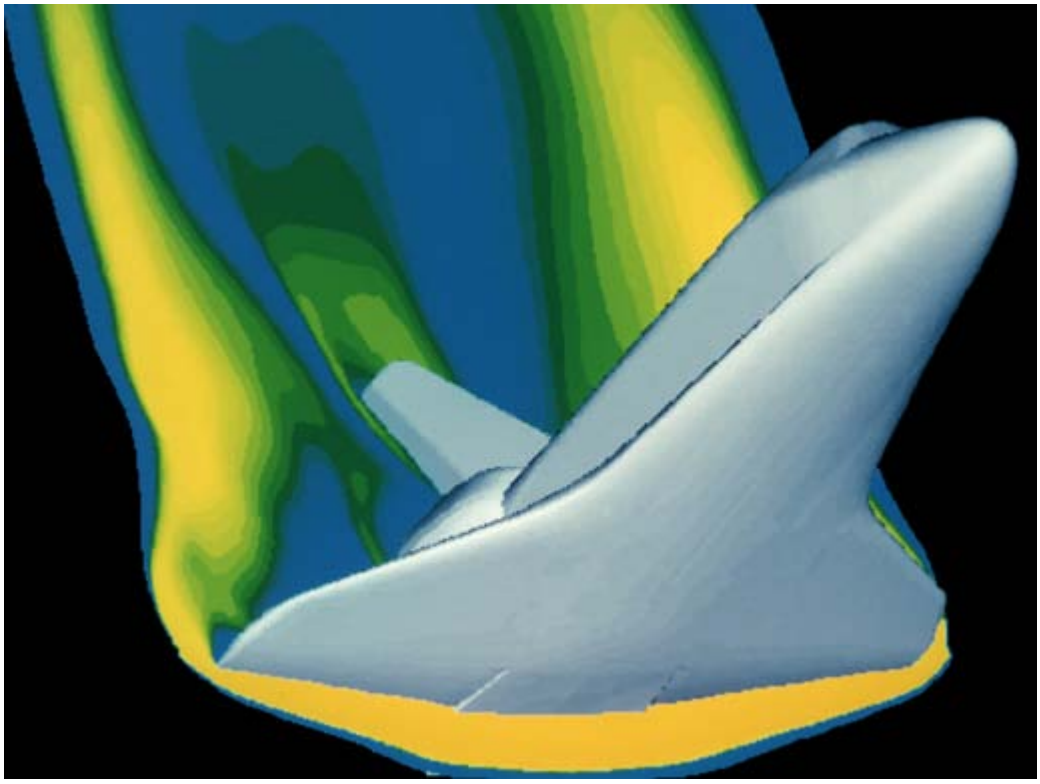
Usually multiple reasonable solutions exist, so engineers must evaluate the different design choices on their merits and choose the solution that best meets their requirements. Genrich Altshuller, after gathering statistics on a large number of patents, suggested that compromises are at the heart of "low-level" engineering designs, while at a higher level the best design is one which eliminates the core contradiction causing the problem.

Engineers typically attempt to predict how well their designs will perform to their specifications prior to full-scale production. They use, among other things: prototypes, scale models, simulations, destructive tests, nondestructive tests, and stress tests. Testing ensures that products will perform as expected.

Engineers as professionals take seriously their responsibility to produce designs that will perform as expected and will not cause unintended harm to the public at large. Engineers typically include a factor of safety in their designs to reduce the risk of unexpected failure. However, the greater the safety factor, the less efficient the design may be.

The study of failed products is known as forensic engineering, and can help the product designer in evaluating his or her design in the light of real conditions. The discipline is of greatest value after disasters, such as bridge collapses, when careful analysis is needed to establish the cause or causes of the failure.

Computer use



A computer simulation of high velocity air flow around the Space Shuttle during re-entry. Solutions to the flow require modelling of the combined effects of the fluid flow and heat equations.

As with all modern scientific and technological endeavors, computers and software play an increasingly important role. As well as the typical business application software there are a number of computer aided applications (Computer-aided technologies) specifically for engineering. Computers can be used to generate models of fundamental physical processes, which can be solved using numerical methods.

One of the most widely used tools in the profession is computer-aided design (CAD) software which enables engineers to create 3D models, 2D drawings, and schematics of their designs. CAD together with Digital mockup (DMU) and CAE software such as finite element method analysis or analytic element method allows engineers to create models of designs that can be analyzed without having to make expensive and time-consuming physical prototypes.

These allow products and components to be checked for flaws; assess fit and assembly; study ergonomics; and to analyze static and dynamic characteristics of systems such as stresses, temperatures, electromagnetic emissions, electrical currents and voltages, digital logic levels, fluid flows, and kinematics. Access and distribution of all this information is generally organized with the use of Product Data Management software.

There are also many tools to support specific engineering tasks such as Computer-aided manufacture (CAM) software to generate CNC machining instructions; Manufacturing Process Management software for production engineering; EDA for printed circuit board

(PCB) and circuit schematics for electronic engineers; MRO applications for maintenance management; and AEC software for civil engineering.

In recent years the use of computer software to aid the development of goods has collectively come to be known as Product Lifecycle Management (PLM).

Social context

Engineering is a subject that ranges from large collaborations to small individual projects. Almost all engineering projects are beholden to some sort of financing agency: a company, a set of investors, or a government. The few types of engineering that are minimally constrained by such issues are pro bono engineering and open design engineering.

By its very nature engineering is bound up with society and human behavior. Every product or construction used by modern society will have been influenced by engineering design. Engineering design is a very powerful tool to make changes to environment, society and economies, and its application brings with it a great responsibility. Many engineering societies have established codes of practice and codes of ethics to guide members and inform the public at large.

Engineering projects can be subject to controversy. Examples from different engineering disciplines include the development of nuclear weapons, the Three Gorges Dam, the design and use of Sport utility vehicles and the extraction of oil. In response, some western engineering companies have enacted serious corporate and social responsibility policies.

Engineering is a key driver of human development. Sub-Saharan Africa in particular has a very small engineering capacity which results in many African nations being unable to develop crucial infrastructure without outside aid. The attainment of many of the Millennium Development Goals requires the achievement of sufficient engineering capacity to develop infrastructure and sustainable technological development.

All overseas development and relief NGOs make considerable use of engineers to apply solutions in disaster and development scenarios. A number of charitable organizations aim to use engineering directly for the good of mankind:

- Engineers Without Borders
- Engineers Against Poverty
- Registered Engineers for Disaster Relief
- Engineers for a Sustainable World

Relationships with other disciplines

Science

Scientists study the world as it is; engineers create the world that has never been.
—Theodore von Kármán

Bioreactors for producing proteins, NRC Biotechnology Research Institute, Montréal, Canada

There exists an overlap between the sciences and engineering practice; in engineering, one applies science. Both areas of endeavor rely on accurate observation of materials and phenomena. Both use mathematics and classification criteria to analyze and communicate observations.

Scientists are expected to interpret their observations and to make expert recommendations for practical action based on those interpretations. Scientists may also have to complete engineering tasks, such as designing experimental apparatus or building prototypes. Conversely, in the process of developing technology engineers sometimes find themselves exploring new phenomena, thus becoming, for the moment, scientists.

In the book *What Engineers Know and How They Know It*, Walter Vincenti asserts that engineering research has a character different from that of scientific research. First, it often deals with areas in which the basic physics and/or chemistry are well understood, but the problems themselves are too complex to solve in an exact manner.

Examples are the use of numerical approximations to the Navier-Stokes equations to describe aerodynamic flow over an aircraft, or the use of Miner's rule to calculate fatigue damage. Second, engineering research employs many semi-empirical methods that are foreign to pure scientific research, one example being the method of parameter variation.

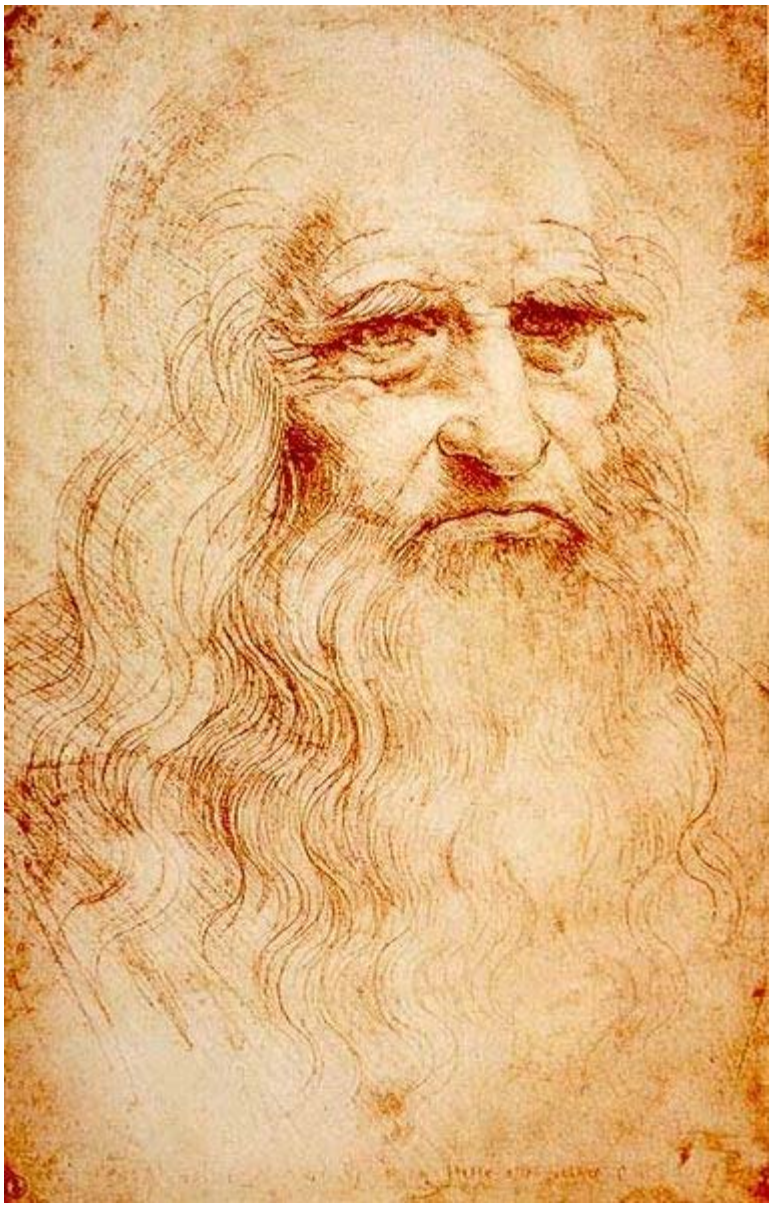
As stated by Fung et al. in the revision to the classic engineering text, Foundations of Solid Mechanics:

"Engineering is quite different from science. Scientists try to understand nature. Engineers try to make things that do not exist in nature. Engineers stress invention. To embody an invention the engineer must put his idea in concrete terms, and design something that people can use. That something can be a device, a gadget, a material, a method, a computing program, an innovative experiment, a new solution to a problem, or an improvement on what is existing. Since a design has to be concrete, it must have its geometry, dimensions, and characteristic numbers. Almost all engineers working on new designs find that they do not have all the needed information. Most often, they are limited by insufficient scientific knowledge. Thus they study mathematics, physics, chemistry,

biology and mechanics. Often they have to add to the sciences relevant to their profession. Thus engineering sciences are born."

Although engineering solutions make use of scientific principles, engineers must also take into account safety, efficiency, economy, reliability and constructibility or ease of fabrication, as well as legal considerations such as patent infringement or liability in the case of failure of the solution.

Medicine and biology



Leonardo da Vinci, seen here in a self-portrait, has been described as the epitome of the artist/engineer. He is also known for his studies on human anatomy and physiognomy

The study of the human body, albeit from different directions and for different purposes, is an important common link between medicine and some engineering disciplines. Medicine aims to sustain, enhance and even replace functions of the human body, if necessary, through the use of technology.

Modern medicine can replace several of the body's functions through the use of artificial organs and can significantly alter the function of the human body through artificial devices such as, for example, brain implants and pacemakers. The fields of Bionics and medical Bionics are dedicated to the study of synthetic implants pertaining to natural systems.

Conversely, some engineering disciplines view the human body as a biological machine worth studying, and are dedicated to emulating many of its functions by replacing biology with technology. This has led to fields such as artificial intelligence, neural networks, fuzzy logic, and robotics. There are also substantial interdisciplinary interactions between engineering and medicine.

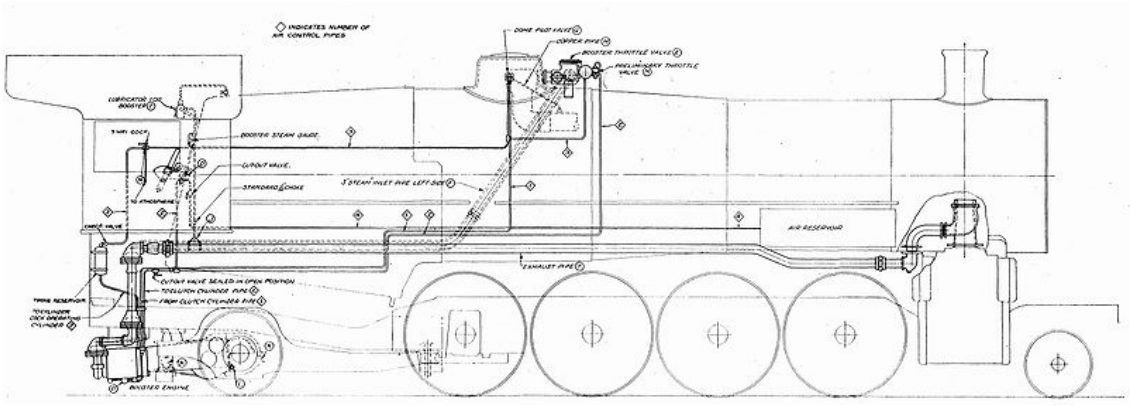
Both fields provide solutions to real world problems. This often requires moving forward before phenomena are completely understood in a more rigorous scientific sense and therefore experimentation and empirical knowledge is an integral part of both.

Medicine, in part, studies the function of the human body. The human body, as a biological machine, has many functions that can be modeled using Engineering methods.

The heart for example functions much like a pump, the skeleton is like a linked structure with levers, the brain produces electrical signals etc. These similarities as well as the increasing importance and application of Engineering principles in Medicine, led to the development of the field of biomedical engineering that uses concepts developed in both disciplines.

Newly emerging branches of science, such as Systems biology, are adapting analytical tools traditionally used for engineering, such as systems modeling and computational analysis, to the description of biological systems.

Art



A drawing for a booster engine for steam locomotives. Engineering is applied to design, with emphasis on function and the utilization of mathematics and science.

There are connections between engineering and art; they are direct in some fields, for example, architecture, landscape architecture and industrial design (even to the extent that these disciplines may sometimes be included in a University's Faculty of Engineering); and indirect in others.

The Art Institute of Chicago, for instance, held an exhibition about the art of NASA's aerospace design. Robert Maillart's bridge design is perceived by some to have been deliberately artistic. At the University of South Florida, an engineering professor, through a grant with the National Science Foundation, has developed a course that connects art and engineering.

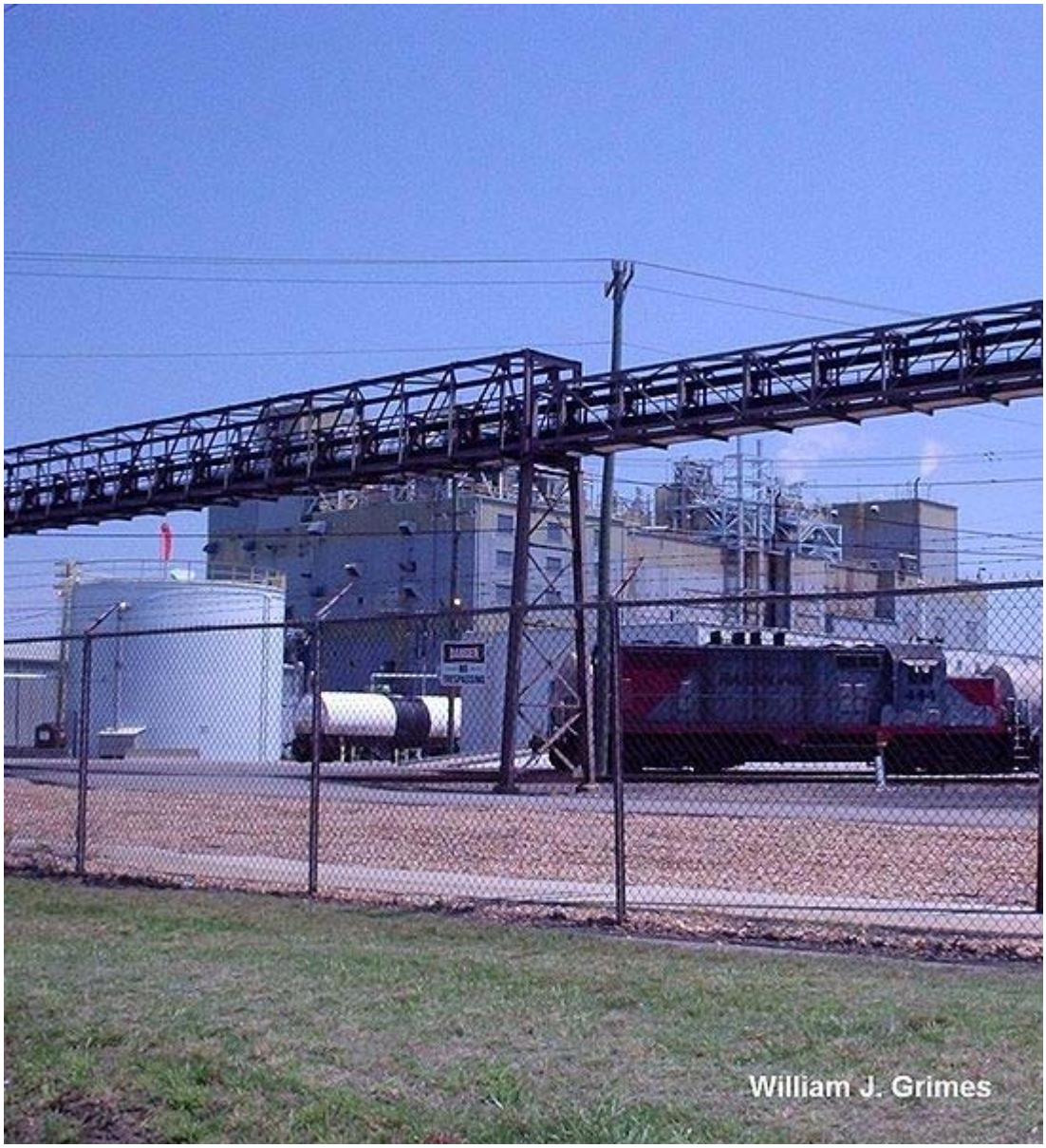
Among famous historical figures Leonardo Da Vinci is a well known Renaissance artist and engineer, and a prime example of the nexus between art and engineering.

Other fields

In Political science the term *engineering* has been borrowed for the study of the subjects of Social engineering and Political engineering, which deal with forming political and social structures using engineering methodology coupled with political science principles. Financial engineering has similarly borrowed the term.

Chapter 4

Chemical Plant



BASF Chemical Plant Portsmouth Site in the West Norfolk area of Portsmouth, Virginia, United States. The plant is served by the Commonwealth Railway.

A **chemical plant** is an industrial process plant that manufactures (or otherwise processes) chemicals, usually on a large scale. The general objective of a chemical plant is to create new material wealth via the chemical or biological transformation and or separation of materials. Chemical plants use special equipment, units, and technology in the processes. Other kinds of plants, such as polymer, pharmaceutical, food, and some beverage production facilities, power plants, oil refineries or other refineries, natural gas processing and biochemical plants, water and wastewater treatment, and pollution control equipment use many technologies which have similarities to chemical plant technology such as fluid systems. Some would consider an oil refinery or a pharmaceutical or polymer manufacturer to be effectively a chemical plant.

Petrochemical plants (plants using petroleum as a raw material) are usually located adjacent to an oil refinery to minimize transportation costs for the feedstocks produced by the refinery. Specialty chemical plants are usually much smaller and not as sensitive to location.

Chemical processes

Chemical plants typically use chemical processes, which are detailed industrial-scale methods, to produce the chemicals. The same chemical process can be used at more than one chemical plant, with possibly differently scaled capacities at each plant. Also, a chemical plant at a site may be constructed to utilize more than one chemical process.

A chemical plant commonly has usually large vessels or sections called **units** that are interconnected by piping or other material-moving equipment which can carry **streams** of material. Such material streams can include fluids (gas or liquid carried in piping) or sometimes solids or mixtures such as slurries. An overall chemical process is commonly made up of steps called unit operations which occur in the individual units. A raw material going into a chemical process or plant as input to be converted into a product is commonly called a **feedstock**, or simply **feed**. In addition to feedstocks for the plant as a whole, an input stream of material to be processed in a particular unit can similarly be considered feed for that unit. Output streams from the plant as a whole are final products and output streams from individual units may be considered intermediate products for their units. However, final products from one plant may be intermediate chemicals used as feedstock in another plant for further processing. For example, some products from an oil refinery may used as feedstock in petrochemical plants.

Either the feedstock(s), the product(s), or both may be individual compounds or mixtures. It is often not worthwhile separating the components in these mixtures completely based on product requirements and economics.

Continuous and batch operation

Chemical processes may be run in continuous or batch operation. In **batch** operation, production occurs in time-sequential steps in batches. A batch of feedstock(s) is fed into a process or unit, then the chemical process takes place, then the product(s) and any other outputs are removed. Such batch production may be repeated over again and again with new batches of feedstock. Batch operation is commonly used in smaller scale plants such as pharmaceutical or specialty chemicals production.

In **continuous** operation, all steps are ongoing continuously in time. During usual continuous operation, the feeding and product removal are ongoing streams of moving material, which together with the process itself, all take place simultaneously and continuously. Chemical plants or units in continuous operation are usually in a steady state or approximate steady state. Steady state means that quantities related to the process do not change as time passes during operation. Such constant quantities include stream flow rates, heating or cooling rates, temperatures, pressures, and chemical compositions at every point (location). Continuous operation is more efficient in many large scale operations like petroleum refineries. It is possible for some units to operate continuously and others be in batch operation in a chemical plant; for example, see Continuous distillation and Batch distillation. The amount of primary feedstock or product per unit of time which a plant or unit can process is referred to as the **capacity** of that plant or unit. For examples: the capacity of an oil refinery may be given in terms of barrels of crude oil refined per day; alternatively chemical plant capacity may be given in tons of product produced per day. In actual daily operation, a plant (or unit) will operate at a percentage of its full capacity.

Units and fluid systems

Various kinds of unit operations are conducted in various kinds of units. Although some units may operate at ambient temperature or pressure, many units operate at higher or lower temperatures or pressures. Vessels in chemical plants are often cylindrical with rounded ends, a shape which can be suited to hold either high pressure or vacuum. Chemical reactions can convert certain kinds of compounds into other compounds in chemical reactors. Chemical reactors may be packed beds and may have solid heterogeneous catalysts which stay in the reactors as fluids move through. Since the surface of solid heterogeneous catalysts may sometimes become poisoned from deposits such as coke, regeneration of catalysts may be necessary. Fluidized beds may also be used in some cases. There can also be units (or subunits) for mixing (including dissolving), separation, heating, cooling, or some combination of these. For example, chemical reactors often have stirring for mixing and heating or cooling going on in them. When designing plants on a large scale, heat produced or absorbed by chemical reactions should be considered. Some plants may have units with organism cultures for biochemical processes such as fermentation or enzyme production.

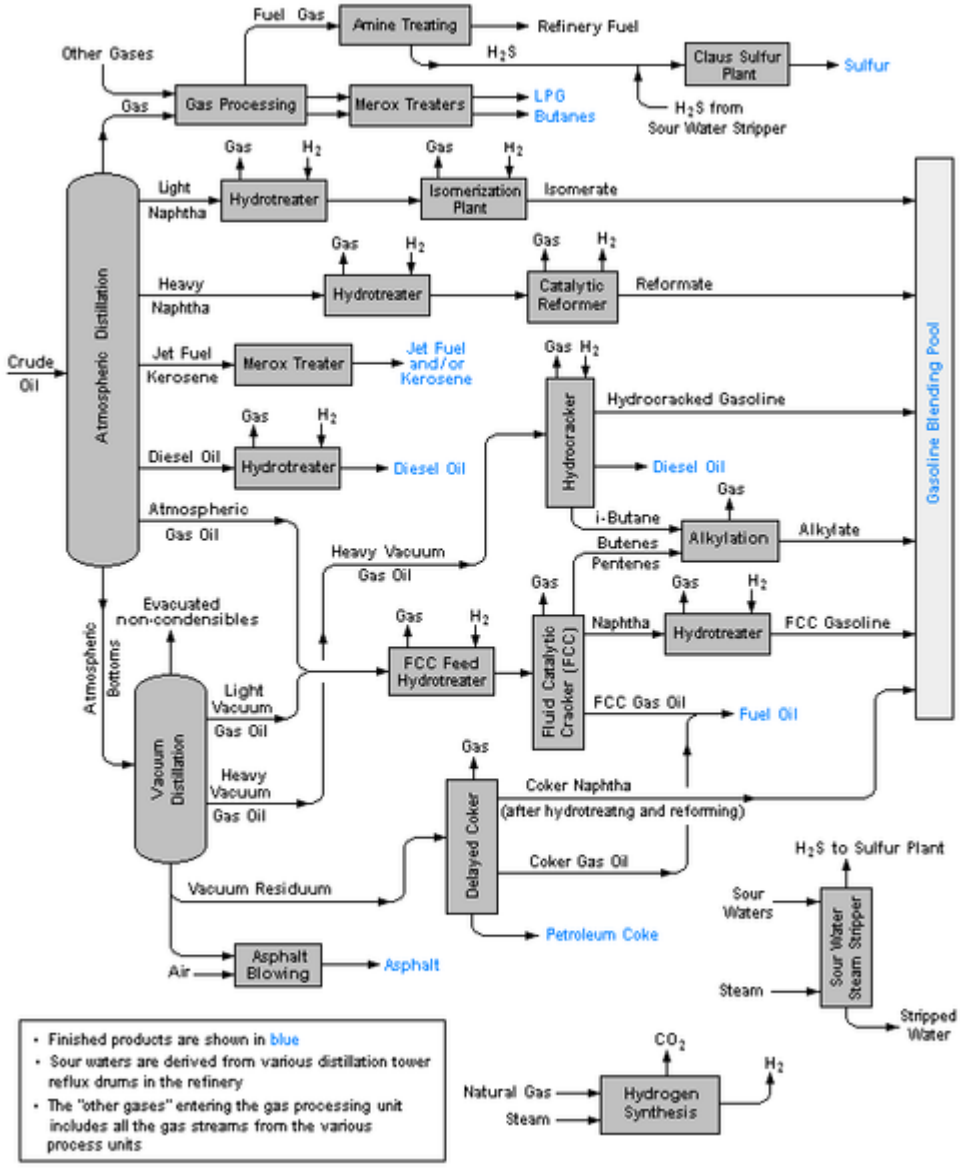
Distillation plant in Italy

Separation processes include filtration, settling (sedimentation), extraction or leaching, distillation, recrystallization or precipitation (followed by filtration or settling), reverse osmosis, drying, and adsorption. Heat exchangers are often used for heating or cooling, including boiling or condensation, often in conjunction with other units such as distillation towers. There may also be storage tanks for storing feedstock, intermediate or final products, or waste. Storage tanks commonly have level indicators to show how full they are. There may be structures holding or supporting sometimes massive units and their associated equipment. There are often stairs, ladders, or other steps for personnel to reach points in the units for sampling, inspection, or maintenance. An area of a plant or facility with numerous storage tanks is sometimes called a *tank farm*, especially at an oil depot.

Fluid systems for carrying liquids and gases include piping and tubing of various diameter sizes, various types of valves for controlling or stopping flow, pumps for moving or pressurizing liquid, and compressors for pressurizing or moving gases.

Vessels, piping, tubing, and sometimes other equipment at high or very low temperature are commonly covered with insulation for personnel safety and to maintain temperature inside. Fluid systems and units commonly have instrumentation such as temperature and pressure sensors and flow measuring devices at select locations in a plant. Online analyzers for chemical or physical property analysis have become more common. Solvents can sometimes be used to dissolve reactants or materials such as solids for extraction or leaching, to provide a suitable medium for certain chemical reactions to run, or so they can otherwise be treated as fluids.

Chemical plant design



Flow diagram for a typical oil refinery

The fundamental aspects of designing chemical plants are done by chemical engineers. In plant design, typically less than 1% of ideas for new designs ever become commercialized. During this solution process, typically, cost studies are used as an initial

screening to eliminate unprofitable designs. If a process appears profitable, then other factors are considered, such as safety, environmental constraints, controllability, etc. The general goal in plant design, is to construct or synthesize “optimum designs” in the neighborhood of the desired constraints.

Many times chemists research chemical reactions or other chemical principles in a laboratory, commonly on a small scale in a "batch-type" experiment. Chemistry information obtained is then used by chemical engineers, along with expertise of their own, to convert to a chemical process and scale up the batch size or capacity. Commonly, a small chemical plant called a pilot plant is built to provide design and operating information before construction of a large plant. From data and operating experience obtained from the pilot plant, a scaled-up plant can be designed for higher or full capacity. After the fundamental aspects of a plant design are determined, mechanical or electrical engineers may become involved with mechanical or electrical details, respectively. Structural engineers may become involved in the plant design to ensure the structures can support the weight of the units, piping, and other equipment.

The units, streams, and fluid systems of chemical plants or processes can be represented by block flow diagrams which are very simplified diagrams, or process flow diagrams which are somewhat more detailed. The streams and other piping are shown as lines with arrow heads showing usual direction of material flow. In block diagrams, units are often simply shown as blocks. Process flow diagrams may use more detailed symbols and show pumps, compressors, and major valves. Likely values or ranges of material flow rates for the various streams are determined based on desired plant capacity using material balance calculations. Energy balances are also done based on heats of reaction, heat capacities, expected temperatures and pressures at various points to calculate amounts of heating and cooling needed in various places and to size heat exchangers. Chemical plant design can be shown in fuller detail in a piping and instrumentation diagram (P&ID) which shows all piping, tubing, valves, and instrumentation, typically with special symbols. Showing a full plant is often complicated in a P&ID, so often only individual units or specific fluid systems are shown in a single P&ID.

In the plant design, the units are sized for the maximum capacity each may have to handle. Similarly, sizes for pipes, pumps, compressors, and associated equipment are chosen for the flow capacity they have to handle. Utility systems such as electric power and water supply should also be included in the plant design. Additional piping lines for non-routine or alternate operating procedures, such as plant or unit startups and shutdowns, may have to be included. Fluid systems design commonly includes isolation valves around various units or parts of a plant so that a section of a plant could be isolated in case of a problem such as a leak in a unit. If pneumatically or hydraulically actuated valves are used, a system of pressurizing lines to the actuators are needed. Any points where process samples may have to be taken should have sampling lines, valves, and access to them included in the detailed design. If necessary, provisions should be made for reducing high pressure or temperature of a sampling stream, such including a pressure reducing valve or sample cooler.

Units and fluid systems in the plant including all vessels, piping, tubing, valves, pumps, compressors, and other equipment must be rated or designed to be able to withstand the entire range of pressures, temperatures, and other conditions which they could possibly encounter, including any appropriate safety factors. All such units and equipment should

also be checked for materials compatibility to ensure they can withstand long-term exposure to the chemicals they will come in contact with. Any closed system in a plant which has a means of pressurizing possibly beyond the rating of its equipment, such as heating, exothermic reactions, or certain pumps or compressors, should have an appropriately sized pressure relief valve included to prevent overpressurization for safety. Frequently all of these parameters (temperatures, pressures, flow, etc.) are exhaustively analyzed in combination through a *Hazop* or *fault tree analysis*, to ensure that the plant has no known risk of serious hazard.

Within any constraints the plant is subject to, design parameters are optimized for good economic performance while ensuring safety and welfare of personnel and the surrounding community. For flexibility, a plant may be designed to operate in a range around some optimal design parameters in case feedstock or economic conditions change and re-optimization is desirable. In more modern times, computer simulations or other computer calculations have been used to help in chemical plant design or optimization.

Plant operation

Process control

In process control, information gathered automatically from various sensors or other devices in the plant is used to control various equipment for running the plant, thereby controlling operation of the plant. Instruments receiving such information signals and sending out control signals to perform this function automatically are process *controllers*. Previously, pneumatic controls were sometimes used. Electrical controls are now common. A plant often has a control room with displays of parameters such as key temperatures, pressures, fluid flow rates and levels, operating positions of key valves, pumps and other equipment, etc. In addition, operators in the control room can control various aspects of the plant operation, often including overriding automatic control. Process control with a computer represents more modern technology. Based on possible changing feedstock composition, changing products requirements or economics, or other changes in constraints, operating conditions may be re-optimized to maximize profit.

Workers

As in any industrial setting, there are a variety of workers working throughout a chemical plant facility, often organized into departments, sections, or other work groups. Such workers typically include engineers, plant operators, and maintenance technicians. Other personnel at the site could include chemists, management/administration and office workers. Types of engineers involved in operations or maintenance may include chemical process engineers, mechanical engineers for maintaining mechanical equipment, and electrical/computer engineers for electrical or computer equipment.

Transport

Large quantities of fluid feedstock or product may enter or leave a plant by pipeline, railroad tank car, or tanker truck. For example, petroleum commonly comes to a refinery by pipeline. Pipelines can also carry petrochemical feedstock from a refinery to a nearby petrochemical plant. Natural gas is a product which comes all the way from a natural gas

processing plant to final consumers by pipeline or tubing. Large quantities of liquid feedstock are typically pumped into process units. Smaller quantities of feedstock or product may be shipped to or from a plant in drums. Use of drums about 55 gallons in capacity is common for packaging industrial quantities of chemicals. Smaller batches of feedstock may be added from drums or other containers to process units by workers.

Maintenance

In addition to feeding and operating the plant, and packaging or preparing the product for shipping, plant workers are needed for taking samples for routine and troubleshooting analysis and for performing routine and non-routine maintenance. Routine maintenance can include periodic inspections and replacement of worn catalyst, analyzer reagents, various sensors, or mechanical parts. Non-routine maintenance can include investigating problems and then fixing them, such as leaks, failure to meet feed or product specifications, mechanical failures of valves, pumps, compressors, sensors, etc.

Statutory and regulatory compliance

When working with chemicals, safety is a concern. In the United States, the law requires that employers provide workers working with chemicals with access to a Material Safety Data Sheet (MSDS) for every kind of chemical they work with. An MSDS for a certain chemical is prepared and provided by the supplier to whoever buys the chemical. Other laws covering chemical safety, hazardous waste, and pollution must be observed, including statutes such as the Resource Conservation and Recovery Act (RCRA) and the Toxic Substances Control Act (TSCA), and regulations such as the Chemical Facility Anti-Terrorism Standards in the United States. Hazmat (hazardous materials) teams are trained to deal with chemical leaks or spills. Process Hazard Analysis (PHA) is used to assess potential hazards in chemical plants. In 1998, the U. S. Chemical Safety and Hazard Investigation Board has become operational.

Plant facilities

The actual production or process part of a plant may be indoors, outdoors, or a combination of the two. The actual production section of a facility usually has the appearance of a rather industrial environment. Hard hats and work shoes are commonly worn. Floors and stairs are often made of metal grating, and there is practically no decoration. There may also be pollution control or waste treatment facilities or equipment. Sometimes existing plants may be expanded or modified based on changing economics, feedstock, or product needs. As in other production facilities, there may be shipping and receiving, and storage facilities. In addition, there are usually certain other facilities, typically indoors, to support production at the site.

Although some simple sample analysis may be able to be done by operations technicians in the plant area, a chemical plant typically has a laboratory where chemists analyze samples taken from the plant. Such analysis can include chemical analysis or determination of physical properties. Sample analysis can include routine quality control on feedstock coming into the plant, intermediate and final products to ensure quality specifications are met. Non-routine samples may be taken and analyzed for investigating plant process problems also. A larger chemical company often has a research laboratory

for developing and testing products and processes where there may be pilot plants, but such a laboratory may be located at a site separate from the production plants.

A plant may also have a workshop or maintenance facility for repairs or keeping maintenance equipment. There is also typically some office space for engineers, management or administration, and perhaps for receiving visitors. The decorum there is commonly more typical of an office environment.

Corrosion and use of new materials

Corrosion in chemical process plants is a big issue that consumes billions of dollars yearly. Electrochemical corrosion of metals is pronounced in chemical process plants due to the presence of acid fumes and other electrolytic interactions. Recently, FRP (Fibre-reinforced plastic) is used as a material of construction. The British standard specification BS4994 is widely used for design and construction of the vessels, tanks, etc.

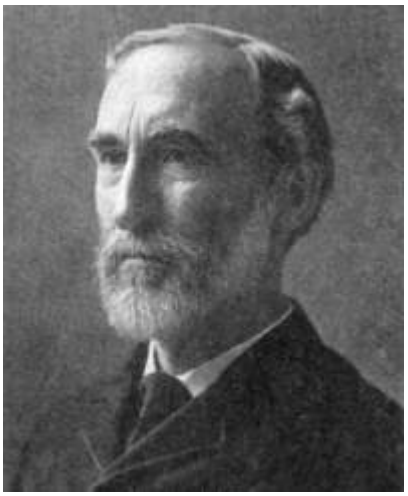
Chapter 5

Chemical Thermodynamics

Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Chemical thermodynamics involves not only laboratory measurements of various thermodynamic properties, but also the application of mathematical methods to the study of chemical questions and the *spontaneity* of processes.

The structure of chemical thermodynamics is based on the first two laws of thermodynamics. Starting from the first and second laws of thermodynamics, four equations called the "fundamental equations of Gibbs" can be derived. From these four, a multitude of equations, relating the thermodynamic properties of the thermodynamic system can be derived using relatively simple mathematics. This outlines the mathematical framework of chemical thermodynamics.

History



J. Willard Gibbs - founder of *chemical thermodynamics*

In 1865, the German physicist Rudolf Clausius, in his *Mechanical Theory of Heat*, suggested that the principles of thermochemistry, e.g. such as the heat evolved in combustion reactions, could be applied to the principles of thermodynamics. Building on the work of Clausius, between the years 1873-76 the American mathematical physicist Willard Gibbs published a series of three papers, the most famous one being the paper *On the Equilibrium of Heterogeneous Substances*. In these papers, Gibbs showed how the first two laws of thermodynamics could be measured graphically and mathematically to determine both the thermodynamic equilibrium of chemical reactions as well as their tendencies to occur or proceed. Gibbs' collection of papers provided the first unified body of thermodynamic theorems from the principles developed by others, such as Clausius and Sadi Carnot.

During the early 20th century, two major publications successfully applied the principles developed by Gibbs to chemical processes, and thus established the foundation of the science of chemical thermodynamics. The first was the 1923 textbook *Thermodynamics and the Free Energy of Chemical Substances* by Gilbert N. Lewis and Merle Randall. This book was responsible for supplanting the chemical affinity for the term free energy in the English-speaking world. The second was the 1933 book *Modern Thermodynamics by the methods of Willard Gibbs* written by E. A. Guggenheim. In this manner, Lewis, Randall, and Guggenheim are considered as the founders of modern chemical thermodynamics because of the major contribution of these two books in unifying the application of thermodynamics to chemistry.

Overview

The primary objective of chemical thermodynamics is the establishment of a criterion for the determination of the feasibility or spontaneity of a given transformation. In this manner, chemical thermodynamics is typically used to predict the energy exchanges that occur in the following processes:

1. Chemical reactions
2. Phase changes
3. The formation of solutions

The following state functions are of primary concern in chemical thermodynamics:

- Internal energy (*U*)
- Enthalpy (*H*).
- Entropy (*S*)
- Gibbs free energy (*G*)

Most identities in chemical thermodynamics arise from application of the first and second laws of thermodynamics, particularly the law of conservation of energy, to these state functions.

The 3 laws of thermodynamics:

1. The energy of the universe is constant.
2. In any spontaneous process, there is always an increase in entropy of the universe
3. The entropy of a perfect crystal at 0 kelvins is zero

Chemical energy

Chemical energy is the potential of a chemical substance to undergo a transformation through a chemical reaction or to transform other chemical substances. Breaking or making of chemical bonds involves energy, which may be either absorbed or evolved from a chemical system.

Energy that can be released (or absorbed) because of a reaction between a set of chemical substances is equal to the difference between the energy content of the products and the reactants. This change in energy is called the change in internal energy of a chemical reaction. Where $\Delta U^\circ_{f\,\mathrm{reactants}}$ is the internal energy of formation of the reactant molecules that can be calculated from the bond energies of the various chemical bonds of the molecules under consideration and $\Delta U^\circ_{f\,\mathrm{products}}$ is the internal energy of formation of the product molecules. The internal energy change of a process is equal to the heat change if it is measured under conditions of constant volume, as in a closed rigid container such as a bomb calorimeter. However, under conditions of constant pressure, as in reactions in vessels open to the atmosphere, the measured heat change is not always equal to the internal energy change, because pressure-volume work also releases or absorbs energy. (The heat change at constant pressure is called the enthalpy change; in this case the enthalpy of formation).

Another useful term is the heat of combustion, which is the energy released due to a combustion reaction and often applied in the study of fuels. Food is similar to hydrocarbon fuel and carbohydrate fuels, and when it is oxidized, its caloric content is similar.

In chemical thermodynamics the term used for the chemical potential energy is chemical potential, and for chemical transformation an equation most often used is the Gibbs-Duhem equation.

Chemical reactions

In most cases of interest in chemical thermodynamics there are internal degrees of freedom and processes, such as chemical reactions and phase transitions, which always create entropy unless they are at equilibrium, or are maintained at a "running equilibrium" through "quasi-static" changes by being coupled to constraining devices, such as pistons or electrodes, to deliver and receive external work. Even for homogeneous "bulk" materials, the free energy functions depend on the composition, as do all the extensive thermodynamic potentials, including the internal energy. If the quantities $\{ N_i \}$, the number of chemical species, are omitted from the formulae, it is impossible to describe compositional changes.

Gibbs function

For a "bulk" (unstructured) system they are the last remaining extensive variables. For an unstructured, homogeneous "bulk" system, there are still various *extensive* compositional variables $\{ N_i \}$ that G depends on, which specify the composition, the amounts of each

chemical substance, expressed as the numbers of molecules present or (dividing by Avogadro's number), the numbers of moles

$$G = G(T, P, \{N_i\}) .$$

For the case where only *PV* work is possible

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

in which μ_i is the chemical potential for the *i*-th component in the system

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_{j\neq i},etc.} .$$

The expression for d*G* is especially useful at constant *T* and *P*, conditions which are easy to achieve experimentally and which approximates the condition in living creatures

$$(dG)_{T,P} = \sum_i \mu_i dN_i .$$

Chemical affinity

While this formulation is mathematically defensible, it is not particularly transparent since one does not simply add or remove molecules from a system. There is always a *process* involved in changing the composition; e.g., a chemical reaction (or many), or movement of molecules from one phase (liquid) to another (gas or solid). We should find a notation which does not seem to imply that the amounts of the components (N_i } can be changed independently. All real processes obey conservation of mass, and in addition, conservation of the numbers of atoms of each kind. Whatever molecules are transferred to or from should be considered part of the "system".

Consequently we introduce an explicit variable to represent the degree of advancement of a process, a progress variable ξ for the *extent of reaction* (Prigogine & Defay, p. 18; Prigogine, pp. 4–7; Guggenheim, p. 37.62), and to the use of the partial derivative $\partial G/\partial\xi$ (in place of the widely used "Δ*G*", since the quantity at issue is not a finite change). The result is an understandable expression for the dependence of d*G* on chemical reactions (or other processes). If there is just one reaction

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi.$$

If we introduce the *stoichiometric coefficient* for the *i-th* component in the reaction

$$\nu_i = \partial N_i/\partial\xi$$

which tells how many molecules of *i* are produced or consumed, we obtain an algebraic expression for the partial derivative

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_i \mu_i \nu_i = -\mathbb{A}$$

where, (De Donder; Progoine & Defay, p. 69; Guggenheim, pp. 37,240), we introduce a concise and historical name for this quantity, the "affinity", symbolized by **A**, as introduced by Théophile de Donder in 1923. The minus sign comes from the fact the affinity was defined to represent the rule that spontaneous changes will ensue only when the change in the Gibbs free energy of the process is negative, meaning that the chemical species have a positive affinity for each other. The differential for *G* takes on a simple form which displays its dependence on compositional change

$$(dG)_{T,P} = -\mathbb{A}\, d\xi \,.$$

If there are a number of chemical reactions going on simultaneously, as is usually the case

$$(dG)_{T,P} = -\sum_k \mathbb{A}_k\, d\xi_k \,.$$

a set of reaction coordinates $\{ \xi_j \}$, avoiding the notion that the amounts of the components (N_i } can be changed independently. The expressions above are equal to zero at thermodynamic equilibrium, while in the general case for real systems, they are negative because all chemical reactions proceeding at a finite rate produce entropy. This can be made even more explicit by introducing the reaction *rates* $\mathrm{d}\xi_j/\mathrm{d}t$. For each and every *physically independent process* (Prigogine & Defay, p. 38; Prigogine, p. 24)

$$\mathbb{A}\, \dot{\xi} \leq 0 \,.$$

This is a remarkable result since the chemical potentials are intensive system variables, depending only on the local molecular milieu. They cannot "know" whether the temperature and pressure (or any other system variables) are going to be held constant over time. It is a purely local criterion and must hold regardless of any such constraints. Of course, it could have been obtained by taking partial derivatives of any of the other fundamental state functions, but nonetheless is a general criterion for ($-T$ times) the entropy production from that spontaneous process; or at least any part of it that is not captured as external work.

We now relax the requirement of a homogeneous “bulk” system by letting the chemical potentials and the affinity apply to any locality in which a chemical reaction (or any other process) is occurring. By accounting for the entropy production due to irreversible processes, the inequality for d*G* is now replace by an equality

$$dG = -SdT + VdP - \sum_k \mathbb{A}_k\, d\xi_k + W'$$

or

$$dG_{T,P} = -\sum_k \mathbb{A}_k \, d\xi_k + W'.$$

Any decrease in the Gibbs function of a system is the upper limit for any isothermal, isobaric work that can be captured in the surroundings, or it may simply be dissipated, appearing as T times a corresponding increase in the entropy of the system and/or its surrounding. Or it may go partly toward doing external work and partly toward creating entropy. The important point is that the *extent of reaction* for a chemical reaction may be coupled to the displacement of some external mechanical or electrical quantity in such a way that one can advance only if the other one also does. The coupling may occasionally be *rigid*, but it is often flexible and variable.

Solutions

In solution chemistry and biochemistry, the Gibbs free energy decrease ($\partial G/\partial \xi$, in molar units, denoted cryptically by ΔG) is commonly used as a surrogate for ($-T$ times) the entropy produced by spontaneous chemical reactions in situations where there is no work being done; or at least no "useful" work; i.e., other than perhaps some $\pm P\mathrm{d}V$. The assertion that all *spontaneous reactions have a negative ΔG* is merely a restatement of the fundamental thermodynamic relation, giving it the physical dimensions of energy and somewhat obscuring its significance in terms of entropy. When there is no useful work being done, it would be less misleading to use the Legendre transforms of the entropy appropriate for constant T, or for constant T and P, the Massieu functions $-F/T$ and $-G/T$ respectively.

Non equilibrium

Generally the systems treated with the conventional chemical thermodynamics are either at equilibrium or near equilibrium. Ilya Prigogine developed the thermodynamic treatment of open systems that are far from equilibrium. In doing so he has discovered phenomena and structures of completely new and completely unexpected types. His generalized, nonlinear and irreversible thermodynamics has found surprising applications in a wide variety of fields.

The non equilibrium thermodynamics has been applied for explaining how ordered structures e.g. the biological systems, can develop from disorder. Even if Onsager's relations are utilized, the classical principles of equilibrium in thermodynamics still show that linear systems close to equilibrium always develop into states of disorder which are stable to perturbations and cannot explain the occurrence of ordered structures.

Prigogine called these systems dissipative systems, because they are formed and maintained by the dissipative processes which take place because of the exchange of energy between the system and its environment and because they disappear if that exchange ceases. They may be said to live in symbiosis with their environment.

The method which Prigogine used to study the stability of the dissipative structures to perturbations is of very great general interest. It makes it possible to study the most

varied problems, such as city traffic problems, the stability of insect communities, the development of ordered biological structures and the growth of cancer cells to mention but a few examples.

System constraints

In this regard, it is crucial to understand the role of walls and other *constraints*, and the distinction between *independent* processes and *coupling*. Contrary to the clear implications of many reference sources, the previous analysis is not restricted to homogenous, isotropic bulk systems which can deliver only $P\mathrm{d}V$ work to the outside world, but applies even to the most structured systems. There are complex systems with many chemical "reactions" going on at the same time, some of which are really only parts of the same, overall process. An *independent* process is one that *could* proceed even if all others were unaccountably stopped in their tracks. Understanding this is perhaps a “thought experiment” in chemical kinetics, but actual examples exist.

A gas reaction which results in an increase in the number of molecules will lead to an increase in volume at constant external pressure. If it occurs inside a cylinder closed with a piston, the equilibrated reaction can proceed only by doing work against an external force on the piston. The extent variable for the reaction can increase only if the piston moves, and conversely, if the piston is pushed inward, the reaction is driven backwards.

Similarly, a redox reaction might occur in an electrochemical cell with the passage of current in wires connecting the electrodes. The half-cell reactions at the electrodes are constrained if no current is allowed to flow. The current might be dissipated as joule heating, or it might in turn run an electrical device like a motor doing mechanical work. An automobile lead-acid battery can be recharged, driving the chemical reaction backwards. In this case as well, the reaction is not an independent process. Some, perhaps most, of the Gibbs free energy of reaction may be delivered as external work.

The hydrolysis of ATP to ADP and phosphate can drive the force times distance work delivered by living muscles, and synthesis of ATP is in turn driven by a redox chain in mitochondria and chloroplasts, which involves the transport of ions across the membranes of these cellular organelles. The coupling of processes here, and in the previous examples, is often not complete. Gas can leak slowly past a piston, just as it can slowly leak out of a rubber balloon. Some reaction may occur in a battery even if no external current is flowing. There is usually a coupling coefficient, which may depend on relative rates, which determines what percentage of the driving free energy is turned into external work, or captured as "chemical work"; a misnomer for the free energy of another chemical process.

Chapter 6

Conservation of Mass

The **law of conservation of mass**, also known as **principle of mass/matter conservation** is that the mass of a closed system (in the sense of a completely isolated system) will remain constant over time. This is much like the conservation of energy in a sense that both keep the energy/mass enclosed in the system (hence, "conservation"). The mass of an isolated system cannot be changed as a result of processes acting inside the system. A similar statement is that mass cannot be created/destroyed, although it may be rearranged in space, and changed into different types of particles. This implies that for any chemical process in a closed system, the mass of the reactants must equal the mass of the products.

Opposed to conservation, the principle of *matter* conservation (in the sense of conservation of particles which are agreed to be "matter") may be considered as an approximate physical law, that is true only in the classical sense, without consideration of special relativity and quantum mechanics. Another difficulty with the idea of conservation of "matter," is that "matter" is not a well-defined word scientifically, and when particles which are considered to be "matter" (such as electrons and positrons) are annihilated to make photons (which are often **not** considered matter) then conservation of matter does not take place, even in isolated systems.

Mass is also not generally conserved in "open" systems (even if only open to heat and work), when various forms of energy are allowed into, or out of, the system. However, the law of mass conservation for **closed** (isolated) systems, as viewed over time from any single inertial frame, continues to be true in modern physics. The reason for this is that relativistic equations show that even "massless" particles such as photons still add mass and energy to closed systems, allowing mass (though not matter) to be conserved in all processes where energy does not escape the system. In relativity, different observers may disagree as to the particular **value** of the mass of a given system, but each observer will agree that this value does not change over time, so long as the system is closed.

The historical concept of both matter and mass conservation is widely used in many fields such as chemistry, mechanics, and fluid dynamics. In relativity, the mass-energy equivalence theorem states that mass conservation is equivalent to energy conservation, which is the first law of thermodynamics.

Historical development and importance

An important idea in ancient Greek philosophy is that "Nothing comes from nothing", so that what exists now has always existed, since no new matter can come into existence where there was none before. An explicit statement of this, along with the further principle that nothing can pass away into nothing, is found in Empedocles (ca. 490–430 BCE): "For it is impossible for anything to come to be from what is not, and it cannot be brought about or heard of that what is should be utterly destroyed". A further principle of conservation was stated by Epicurus (341–270 BCE) who, describing the nature of the universe, wrote that "the totality of things was always such as it is now, and always will be". Jain philosophy, which is a non-creationist philosophy and based on teachings of Mahavira (6th century BCE), states that universe and its constituents like matter cannot be destroyed or created. The Jain text Tattvarthasutra (2nd Century) states that a substance is permanent, but its modes are characterised by creation and destruction. A principle of the conservation of matter was also stated by Nasīr al-Dīn al-Tūsī (1201–1274) during the 13th century. He wrote that "A body of matter cannot disappear completely. It only changes its form, condition, composition, color and other properties and turns into a different complex or elementary matter".

The principle of conservation of mass was first outlined clearly by Antoine Lavoisier (1743–1794). It has been claimed that Mikhail Lomonosov (1711–1765) had expressed similar ideas during 1748—and proven them by experiments—but this has been challenged. Others who anticipated the work of Lavoisier include Joseph Black (1728–1799), Henry Cavendish (1731–1810), and Jean Rey (1583–1645).

Historically, the conservation of mass and weight was obscure for millennia because of the buoyant effect of the Earth's atmosphere on the weight of gases. For example, since a piece of wood weighs less after burning, this seemed to suggest that some of its mass disappears, or is transformed or lost. These effects were not understood until careful experiments in which chemical reactions such as rusting were performed in sealed glass ampules, whereby it was found that the chemical reaction did not change the weight of the sealed container. The vacuum pump also helped to allow the effective weighing of gases using scales.

Once understood, the conservation of mass was of great importance in changing alchemy to modern chemistry. When chemists realized that substances never disappeared from measurement with the scales (once buoyancy effects were held constant, or had otherwise been accounted for), they could for the first time embark on quantitative studies of the transformations of substances. This in turn produced ideas of chemical elements, as well as the idea that all chemical processes and transformations (including both fire and metabolism) are simple reactions between invariant amounts or weights of these elements.

Generalization

In special relativity, the conservation of mass does not apply if the system is open and energy escapes. However, it does continue to apply to closed systems.

The mass associated with chemical amounts of energy is too small to measure

The change in mass of certain kinds of open systems where atoms or massive particles are not allowed to escape, but other types of energy (such as light or heat) were allowed to enter or escape, went unnoticed during the 19th century, because the mass-change associated with addition or loss of the fractional amounts of heat and light associated with chemical reactions, was very small. (In theory, mass would not change at all for experiments conducted in closed systems).

In relativity, the theoretical association of all energy with mass was made by Albert Einstein in 1905. However, Max Planck first pointed out that the change in mass of systems for which the chemical amounts of energy were allowed in or out of systems, as predicted by Einstein's theory, was so small that it could not be measured with available instruments, even if it was sought as a test of relativity. Einstein in turn speculated that the energies associated with **radioactive phenomena** were so large as compared with the mass of systems producing them, that they might be measured as loss of fractional mass in systems, once the energy had been removed. This later indeed proved to be possible, although it was eventually to be the first artificial nuclear transmutation reactions in the 1930s, using cyclotrons, that proved a successful test of Einstein's theory regarding mass-loss with energy-loss.

Mass conservation remains correct if energy is not lost

The conservation of relativistic mass implies the viewpoint of a single observer (or the view from a single inertial frame) since changing inertial frames may result in a change of the total energy (relativistic energy) for systems, and this quantity determines the relativistic mass.

The principle that the mass of a system of particles must be equal to the sum of their rest masses, even though true in classical physics, may be false in special relativity. The reason that rest masses cannot be simply added is that this does not take into account other forms of energy, such as kinetic and potential energy, and massless particles such as photons, all of which may (or may not) affect the mass of systems. For moving massive particles in a system, examining the rest masses of the various particles also amounts to introducing many different inertial observation frames (which is prohibited if total system system energy and momentum are to be conserved), and also when in the rest frame of one particle, this procedure ignores the momenta of other particles, which affect the system mass if the other particles are in motion in this frame.

For the special type of mass called invariant mass, changing the inertial frame of observation for a whole closed system has no effect on the measure of invariant mass of the system, which remains both conserved and invariant even for different observers who view the entire system. Invariant mass is a system combination of energy and momentum, which is invariant for any observer, because in any inertial frame, the energies and momenta of the various particles always add to the same quantity. The invariant mass is the relativistic mass of the system when viewed in the center of momentum frame. It is the minimum mass which a system may exhibit in all possible inertial frames.

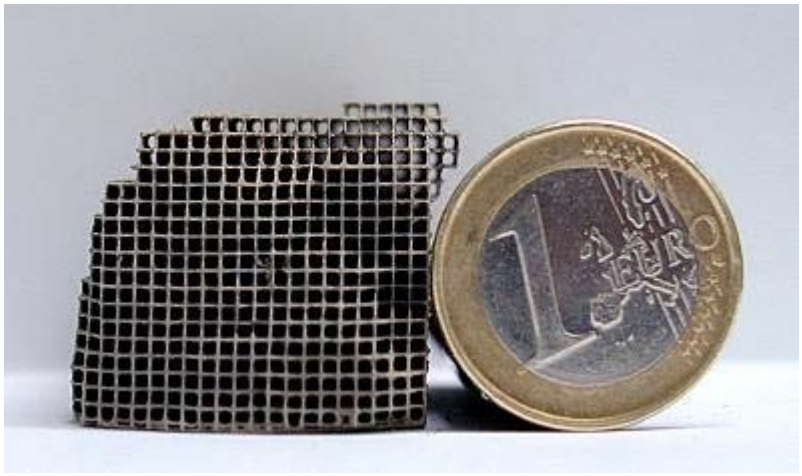
The conservation of both relativistic and invariant mass applies even to systems of particles created by pair production, where energy for new particles may come from kinetic energy of other particles, or from a photon as part of a system. Again, neither the relativistic nor the invariant mass of closed systems changes when new particles are created. However, different inertial observers will disagree on the value of this conserved mass, if it is the relativistic mass. However, all observers agree on the value of the conserved mass, if the mass being measured is the invariant mass.

The mass-energy equivalence formula requires closed systems, since if energy is allowed to escape a system, both relativistic mass and invariant mass will escape also.

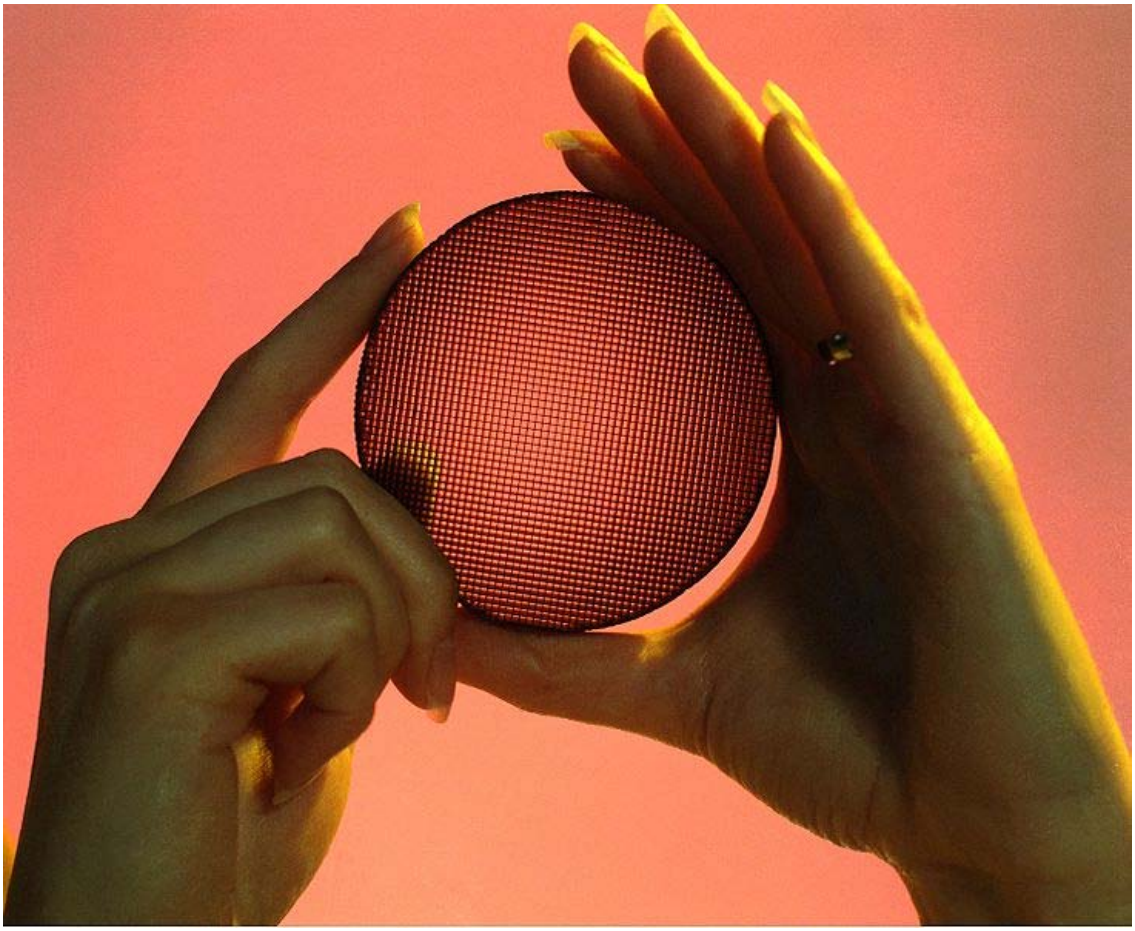
The formula implies that bound systems have an invariant mass (rest mass for the system) less than the sum of their parts, if the binding energy has been allowed to escape the system after the system has been bound. This may happen by converting system potential energy into some other kind of active energy, such as kinetic energy or photons, which easily escape a bound system. The difference in system masses, called a mass defect, is a measure of the binding energy in bound systems — in other words, the energy needed to break the system apart. The greater the mass defect, the larger the binding energy. The binding energy (which itself has mass) must be released (as light or heat) when the parts combine to form the bound system, and this is the reason the mass of the bound system decreases when the energy leaves the system. The total invariant mass is actually conserved, when the mass of the binding energy that has escaped, is taken into account.

Chapter 7

Catalysis



Solid heterogeneous catalysts such as in automobile catalytic converters are plated on structures designed to maximize their surface area.



A low-temperature oxidation catalyst used to convert carbon monoxide to non-toxic carbon dioxide at room temperature. It can also remove formaldehyde from the air.

Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. A catalyst may participate in multiple chemical transformations. Catalysts that speed the reaction are called positive catalysts. Substances that interact with catalysts to slow the reaction are called inhibitors (or negative catalysts). Substances that increase the activity of catalysts are called promoters, and substances that deactivate catalysts are called catalytic poisons.

Catalytic reactions have a lower rate-limiting free energy of activation than the corresponding uncatalyzed reaction, resulting in higher reaction rate at the same temperature. However, the mechanistic explanation of catalysis is complex. Catalysts may affect the reaction environment favorably, or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds, or form specific intermediates that are not produced naturally, such as osmate esters in osmium tetroxide-catalyzed dihydroxylation of alkenes, or cause lysis of reagents to reactive forms, such as atomic hydrogen in catalytic hydrogenation.

Kinetically, catalytic reactions are typical chemical reactions, i.e. the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slowest step, and rates are limited by amount of catalyst and its "activity". In heterogeneous catalysis, the diffusion of reagents to the surface and

diffusion of products from the surface can be rate determining. Analogous events associated with substrate binding and product dissociation apply to homogeneous catalysts.

Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated or destroyed by secondary processes. In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid-liquid system or evaporate in a solid-gas system.

Background

The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant processes are catalysed. Research into catalysis is a major field in applied science and involves many areas of chemistry, notably in organometallic chemistry and materials science. Catalysis is relevant to many aspects of environmental science, e.g. the catalytic converter in automobiles and the dynamics of the ozone hole. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated, as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. The most common catalyst is the proton (H^+). Many transition metals and transition metal complexes are used in catalysis as well. Catalysts called enzymes are important in biology.

A catalyst works by providing an alternative reaction pathway to the reaction product. The rate of the reaction is increased as this alternative route has a lower activation energy than the reaction route not mediated by the catalyst. The disproportionation of hydrogen peroxide to give water and oxygen is a reaction that is strongly affected by catalysts:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$$

This reaction is favoured in the sense that reaction products are more stable than the starting material, however the uncatalysed reaction is slow. The decomposition of hydrogen peroxide is in fact so slow that hydrogen peroxide solutions are commercially available. Upon the addition of a small amount of manganese dioxide, the hydrogen peroxide rapidly reacts according to the above equation. This effect is readily seen by the effervescence of oxygen. The manganese dioxide may be recovered unchanged, and re-used indefinitely, and thus is not consumed in the reaction. Accordingly, manganese dioxide *catalyses* this reaction.

General principles of catalysis

Typical mechanism

Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst. The following is a typical reaction scheme, where ***C*** represents the catalyst, X and Y are reactants, and Z is the product of the reaction of X and Y:

$$X + \boldsymbol{C} \rightarrow X\boldsymbol{C} \quad (1)$$

$$Y + X\boldsymbol{C} \rightarrow XY\boldsymbol{C} \ (2)$$
$$XY\boldsymbol{C} \rightarrow \boldsymbol{C}Z \ (3)$$
$$\boldsymbol{C}Z \rightarrow \boldsymbol{C} + Z \ (4)$$

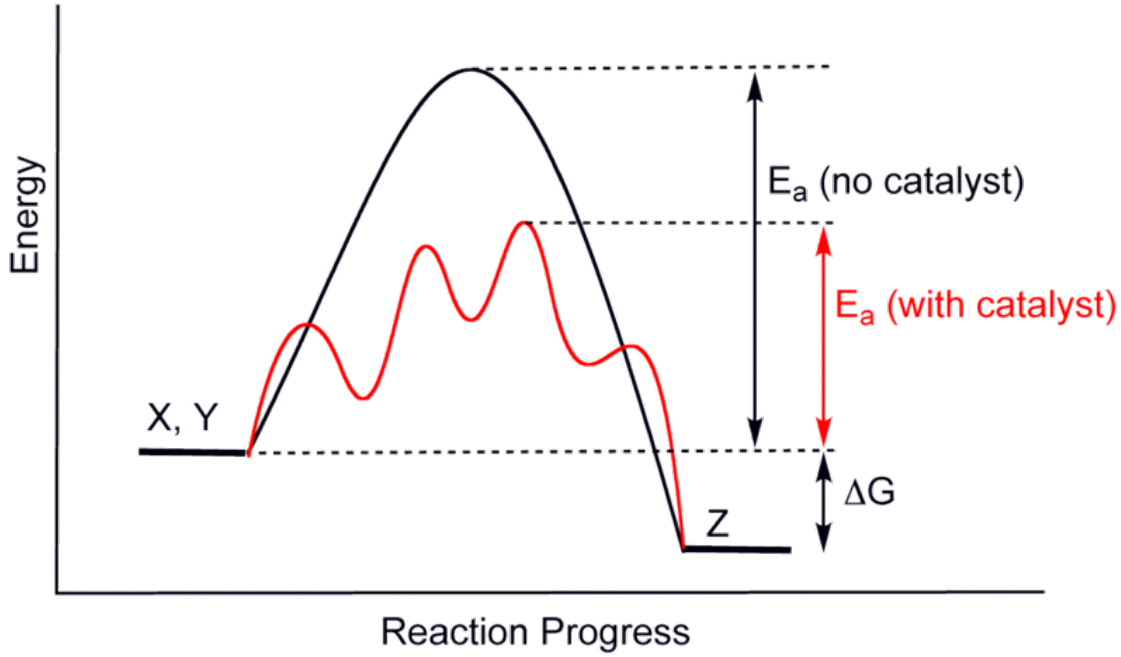
Although the catalyst is consumed by reaction 1, it is subsequently produced by reaction 4, so for the overall reaction:

$$X + Y \rightarrow Z$$

As a catalyst is regenerated in a reaction, often only small amounts are needed to increase the rate of the reaction. In practice, however, catalysts are sometimes consumed in secondary processes.

As an example of this process, in 2008 Danish researchers first revealed the sequence of events when oxygen and hydrogen combine on the surface of titanium dioxide (TiO_2, or *titania*) to produce water. With a time-lapse series of scanning tunneling microscopy images, they determined the molecules undergo adsorption, dissociation and diffusion before reacting. The intermediate reaction states were: HO_2, H_2O_2, then H_3O_2 and the final reaction product (water molecule dimers), after which the water molecule desorbs from the catalyst surface.

Catalysis and reaction energetics



Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical reaction X + Y to give Z. The presence of the catalyst opens a different reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.

Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that

would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures. This effect can be illustrated with a Boltzmann distribution and energy profile diagram.

In the catalyzed elementary reaction, catalysts do **not** change the extent of a reaction: they have **no** effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected. The fact that a catalyst does not change the equilibrium is a consequence of the second law of thermodynamics. Suppose there was such a catalyst that shifted an equilibrium. Introducing the catalyst to the system would result in reaction to move to the new equilibrium, producing energy. Production of energy is a necessary result since reactions are spontaneous if and only if Gibbs free energy is produced, and if there is no energy barrier, there is no need for a catalyst. Then, removing the catalyst would also result in reaction, producing energy; i.e. the addition and its reverse process, removal, would both produce energy. Thus, a catalyst that could change the equilibrium would be a perpetual motion machine, a contradiction to the laws of thermodynamics.

If a catalyst **does** change the equilibrium, then it must be consumed as the reaction proceeds, and thus it is also a reactant. Illustrative is the base-catalysed hydrolysis of esters, where the produced carboxylic acid immediately reacts with the base catalyst and thus the reaction equilibrium is shifted towards hydrolysis.

The SI derived unit for measuring the **catalytic activity** of a catalyst is the katal, which is moles per second. The productivity of a catalyst can be described by the turn over number (or TON) and the catalytic activity by the *turn over frequency* (TOF), which is the TON per time unit. The biochemical equivalent is the enzyme unit.

The catalyst stabilizes the transition state more than it stabilizes the starting material. It decreases the kinetic barrier by decreasing the *difference* in energy between starting material and transition state.

Typical catalytic materials

The chemical nature of catalysts is as diverse as catalysis itself, although some generalizations can be made. Proton acids are probably the most widely used catalysts, especially for the many reactions involving water, including hydrolysis and its reverse. Multifunctional solids often are catalytically active, e.g. zeolites, alumina, higher-order oxides, graphitic carbon, nanoparticles, nanodots, and facets of bulk materials. Transition metals are often used to catalyze redox reactions (oxidation, hydrogenation). Many catalytic processes, especially those used in organic synthesis, require so called "late transition metals", which include palladium, platinum, gold, ruthenium, rhodium, and iridium.

Some so-called catalysts are really **precatalysts**. Precatalysts convert to catalysts in the reaction. For example, Wilkinson's catalyst $RhCl(PPh_3)_3$ loses one triphenylphosphine ligand before entering the true catalytic cycle. Precatalysts are easier to store but are easily activated in situ. Because of this preactivation step, many catalytic reactions involve an induction period.

Chemical species that improve catalytic activity are called **co-catalysts** (**cocatalysts**) or **promotors** in **cooperative catalysis**.

Types of catalysis

Catalysts can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate. Biocatalysts (enzymes) are often seen as a separate group.

Heterogeneous catalysts

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place (Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen). The total surface area of solid has an important effect on the reaction rate. The smaller the catalyst particle size, the larger the surface area for a given mass of particles.

For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto "active sites" on the iron particles. Once adsorbed, the bonds within the reacting molecules are weakened, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is weakened and the hydrogen and nitrogen atoms combine faster than would be the case in the gas phase, so the rate of reaction increases. Another place where an Heterogeneous Catalyst is applied is in Contact Process.

Heterogeneous catalysts are typically “supported,” which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. More often, the support and the catalyst interact, affecting the catalytic reaction. Supports are porous materials with a high surface area, most commonly alumina or various kinds of carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulfate.

Homogeneous catalysts

Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of H^+ on the esterification of esters, e.g. methyl acetate from acetic acid and methanol. For inorganic chemists, homogeneous catalysis is often synonymous with organometallic catalysts.

Electrocatalysts

In the context of electrochemistry, specifically in fuel cell engineering, various metal-containing catalysts are used to enhance the rates of the half reactions that comprise the fuel cell. One common type of fuel cell electrocatalyst is based upon nanoparticles of

platinum that are supported on slightly larger carbon particles. When in contact with one of the electrodes in a fuel cell, this platinum increases the rate of oxygen reduction to water, either to hydroxide or hydrogen peroxide.

Organocatalysis

Whereas transition metals sometimes attract most of the attention in the study of catalysis, small organic molecules without metals can also exhibit catalytic properties, as is apparent from the fact that many enzymes lack transition metals. Typically, organic catalysts require a higher loading (amount of catalyst per unit amount of reactant, expressed in mol% amount of substance) than transition metal(-ion)-based catalysts, but these catalysts are usually commercially available in bulk, helping to reduce costs. In the early 2000s, these organocatalysts were considered "new generation" and are competitive to traditional metal(-ion)-containing catalysts. Organocatalysts are supposed to operate akin to metal-free enzymes utilizing, e.g., non-covalent interactions such as hydrogen bonding. The discipline organocatalysis is divided in the application of covalent (e.g., proline, DMAP) and non-covalent (e.g., thiourea organocatalysis) organocatalysts referring to the preferred catalyst-substrate binding and interaction, respectively.

Significance of catalysis

Estimates are that 90% of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture. In 2005, catalytic processes generated about $900 billion in products worldwide. Catalysis is so pervasive that subareas are not readily classified. Some areas of particular concentration are surveyed below.

Energy processing

Petroleum refining makes intensive use of catalysis for alkylation, catalytic cracking (breaking long-chain hydrocarbons into smaller pieces), naphtha reforming and steam reforming (conversion of hydrocarbons into synthesis gas). Even the exhaust from the burning of fossil fuels is treated via catalysis: Catalytic converters, typically composed of platinum and rhodium, break down some of the more harmful byproducts of automobile exhaust.

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2$$

With regard to synthetic fuels, an old but still important process is the Fischer-Tropsch synthesis of hydrocarbons from synthesis gas, which itself is processed via water-gas shift reactions, catalysed by iron. Biodiesel and related biofuels require processing via both inorganic and biocatalysts.

Fuel cells rely on catalysts for both the anodic and cathodic reactions.

Bulk chemicals

Some of the largest-scale chemicals are produced via catalytic oxidation, often using oxygen. Examples include nitric acid (from ammonia), sulfuric acid (from sulfur dioxide

to sulfur trioxide by the chamber process), terephthalic acid from p-xylene, and acrylonitrile from propane and ammonia.

Many other chemical products are generated by large-scale reduction, often via hydrogenation. The largest-scale example is ammonia, which is prepared via the Haber process from nitrogen. Methanol is prepared from carbon monoxide.

Bulk polymers derived from ethylene and propylene are often prepared via Ziegler-Natta catalysis. Polyesters, polyamides, and isocyanates are derived via acid-base catalysis.

Most carbonylation processes require metal catalysts, examples include the Monsanto acetic acid process and hydroformylation.

Fine chemicals

Many fine chemicals are prepared via catalysis; methods include those of heavy industry as well as more specialized processes that would be prohibitively expensive on a large scale. Examples include olefin metathesis using Grubbs' catalyst, the Heck reaction, and Friedel-Crafts reactions.

Because most bioactive compounds are chiral, many pharmaceuticals are produced by enantioselective catalysis (catalytic asymmetric synthesis).

Food processing

One of the most obvious applications of catalysis is the hydrogenation (reaction with hydrogen gas) of fats using nickel catalyst to produce margarine. Many other foodstuffs are prepared via biocatalysis.

Biology

In nature, enzymes are catalysts in metabolism and catabolism. Most biocatalysts are protein-based, i.e. enzymes, but other classes of biomolecules also exhibit catalytic properties including ribozymes, and synthetic deoxyribozymes.

Biocatalysts can be thought of as intermediate between homogenous and heterogeneous catalysts, although strictly speaking soluble enzymes are homogeneous catalysts and membrane-bound enzymes are heterogeneous. Several factors affect the activity of enzymes (and other catalysts) including temperature, pH, concentration of enzyme, substrate, and products. A particularly important reagent in enzymatic reactions is water, which is the product of many bond-forming reactions and a reactant in many bond-breaking processes.

Enzymes are employed to prepare many commodity chemicals including high-fructose corn syrup and acrylamide.

In the environment

Catalysis impacts the environment by increasing the efficiency of industrial processes, but catalysis also plays a direct role in the environment. A notable example is the

catalytic role of chlorine free radicals in the breakdown of ozone. These radicals are formed by the action of ultraviolet radiation on chlorofluorocarbons (CFCs).

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2$$
$$ClO^{\cdot} + O^{\cdot} \rightarrow Cl^{\cdot} + O_2$$

History

In a general sense, anything that increases the rate of a process is a "catalyst", a term derived from Greek καταλύειν, meaning "to annul," or "to untie," or "to pick up." The phrase *catalysed processes* was coined by Jöns Jakob Berzelius in 1836 to describe reactions that are accelerated by substances that remain unchanged after the reaction. Other early chemists involved in catalysis were Alexander Mitscherlich who referred to *contact processes* and Johann Wolfgang Döbereiner who spoke of *contact action* and whose lighter based on hydrogen and a platinum sponge became a huge commercial success in the 1820s. Humphry Davy discovered the use of platinum in catalysis. In the 1880s, Wilhelm Ostwald at Leipzig University started a systematic investigation into reactions that were catalyzed by the presence of acids and bases, and found that chemical reactions occur at finite rates and that these rates can be used to determine the strengths of acids and bases. For this work, Ostwald was awarded the 1909 Nobel Prize in Chemistry.

Inhibitors, poisons and promoters

Substances that reduce the action of catalysts are called catalyst inhibitors if reversible, and catalyst poisons if irreversible. Promoters are substances that increase the catalytic activity, even though they are not catalysts by themselves.

Inhibitors are sometimes referred to as "negative catalysts" since they decrease the reaction rate. However they do not work by introducing a reaction path with higher activation energy, as this term might suggest; this would not reduce the rate since the reaction would continue to occur by the non-catalyzed path. Instead they act either by inactivating catalysts, or by removing reaction intermediates such as free radicals.

The inhibitor may modify selectivity in addition to rate. For instance, in the reduction of ethyne to ethene, the catalyst is palladium (Pd) partly "poisoned" with lead(II) acetate ($Pb(CH_3COO)_2$). Without the deactivation of the catalyst, the ethene produced will be further reduced to ethane.

The inhibitor can produce this effect by e.g. selectively poisoning only certain types of active sites. Another mechanism is the modification of surface geometry. For instance, in hydrogenation operations, large planes of metal surface function as sites of hydrogenolysis catalysis while sites catalyzing hydrogenation of unsaturates are smaller. Thus, a poison that covers surface randomly will tend to reduce the number of uncontaminated large planes but leave proportionally more smaller sites free, thus changing the hydrogenation vs. hydrogenolysis selectivity. Many other mechanisms are also possible.

Promoters can cover up surface to prevent production of a mat of coke, or even actively remove such material (e.g. rhenium on platinum in platforming). They can aid the dispersion of the catalytic material or bind to reagents.

Current market

The global demand on catalysts in 2007 was estimated at approximately 850 thousand tonnes. The market in volume is expected to grow by 3.5-4% annually through 2012, while the market in value will develop much faster. Surging price of precious metals (e.g. platinum and rhodium) is a main contributor to the rapidly growing catalysts market in value. The market is experiencing influences from environmental regulations, rising raw material prices, call for green chemistry, etc. It is a dramatically changing market with opportunities and risks.

Chapter 8

Crystallization

Crystallization is the (natural or artificial) process of formation of solid crystals precipitating from a solution, melt or more rarely deposited directly from a gas. Crystallization is also a chemical solid-liquid separation technique, in which mass transfer of a solute from the liquid solution to a pure solid crystalline phase occurs. In chemical engineering crystallization occurs in a crystallizator. Crystallization is therefore an aspect of precipitation, obtained through a variation of the solubility conditions of the solute in the solvent, as compared to precipitation due to chemical reaction.

Frost crystallization on a shrub.

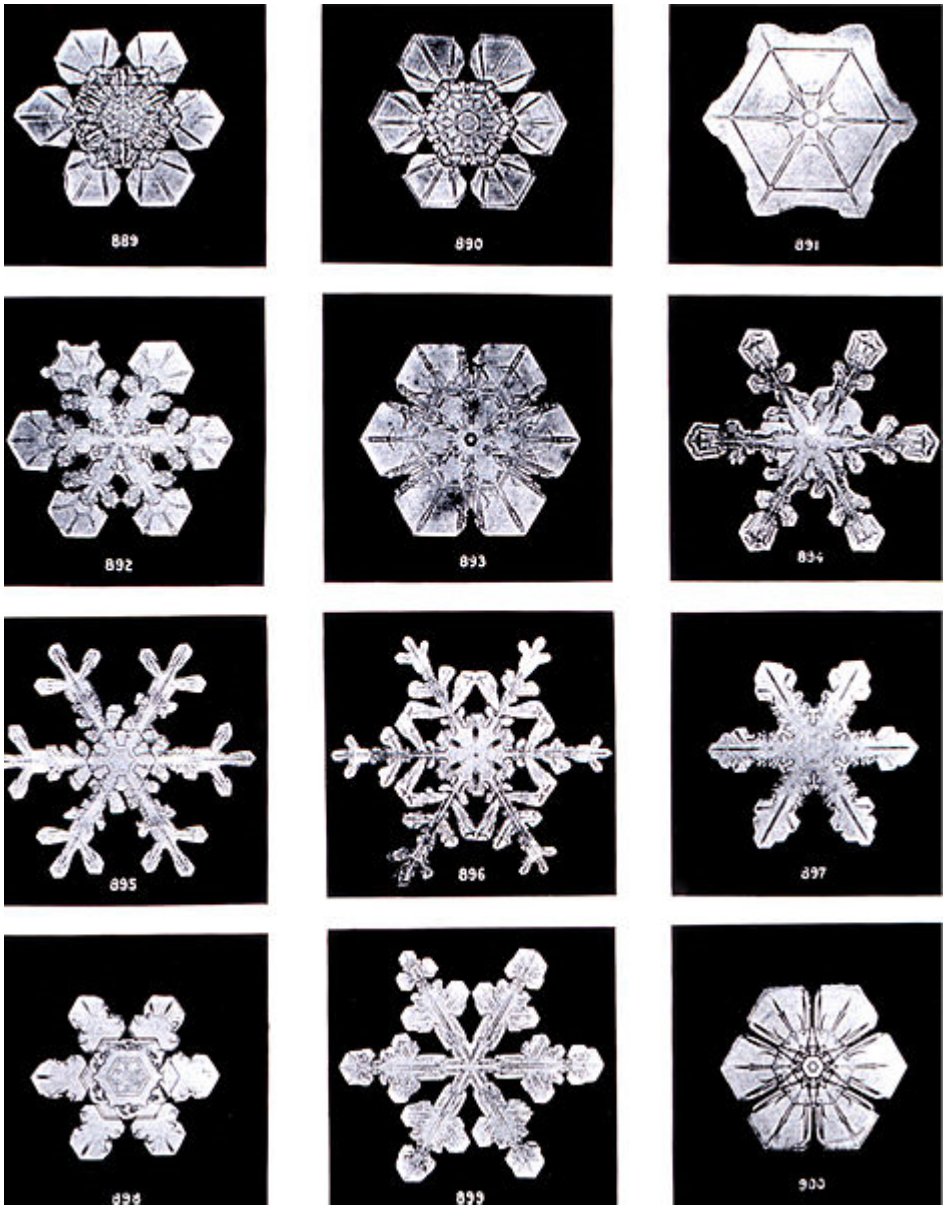
Process

The crystallization process consists of two major events, *nucleation* and *crystal growth*. *Nucleation* is the step where the solute molecules dispersed in the solvent start to gather into clusters, on the nanometer scale (elevating solute concentration in a small region), that become stable under the current operating conditions. These stable clusters constitute the nuclei. However, when the clusters are not stable, they redissolve. Therefore, the clusters need to reach a critical size in order to become stable nuclei. Such critical size is dictated by the operating conditions (temperature, supersaturation, etc.). It is at the stage of nucleation that the atoms arrange in a defined and periodic manner that defines the crystal structure — note that "crystal structure" is a special term that refers to the relative arrangement of the atoms, not the macroscopic properties of the crystal (size and shape), although those are a result of the internal crystal structure.

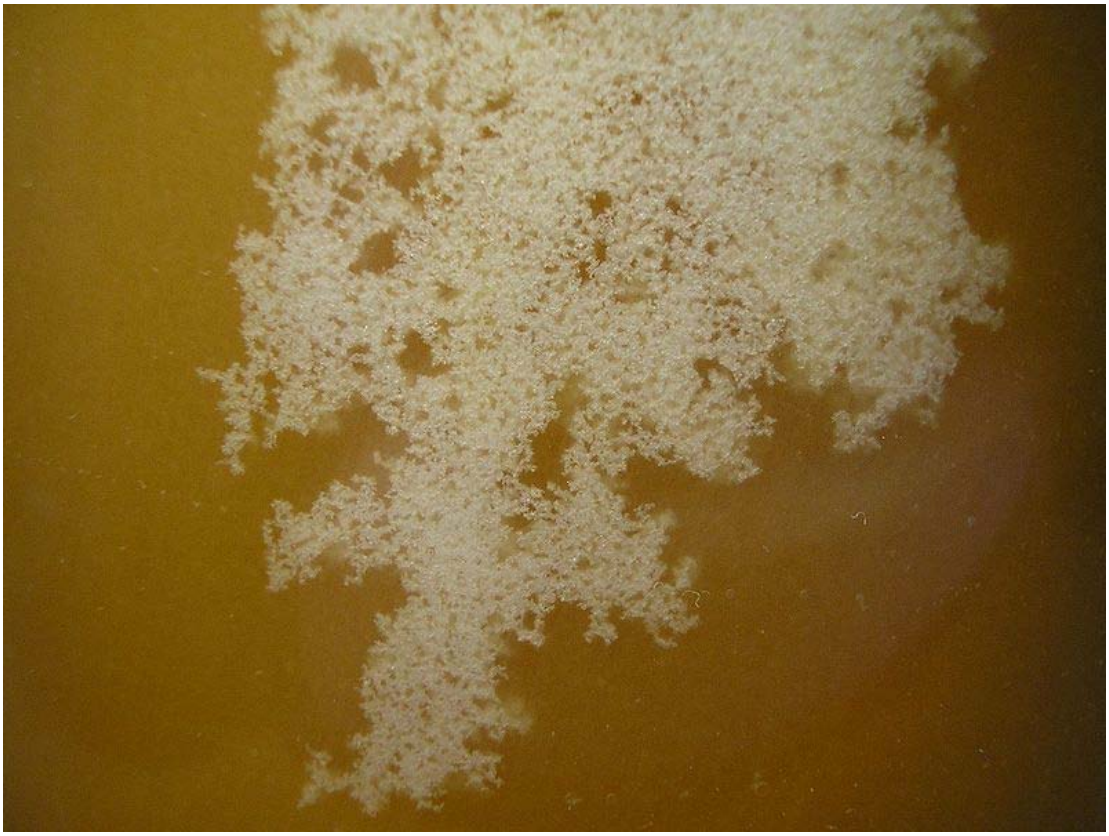
The *crystal growth* is the subsequent growth of the nuclei that succeed in achieving the critical cluster size. Nucleation and growth continue to occur simultaneously while the supersaturation exists. Supersaturation is the driving force of the crystallization, hence the rate of nucleation and growth is driven by the existing supersaturation in the solution. Depending upon the conditions, either nucleation or growth may be predominant over the other, and as a result, crystals with different sizes and shapes are obtained (control of crystal size and shape constitutes one of the main challenges in industrial manufacturing, such as for pharmaceuticals). Once the supersaturation is exhausted, the solid-liquid system reaches equilibrium and the crystallization is complete, unless the operating conditions are modified from equilibrium so as to supersaturate the solution again.

Many compounds have the ability to crystallize with different crystal structures, a phenomenon called polymorphism. Each polymorph is in fact a different thermodynamic solid state and crystal polymorphs of the same compound exhibit different physical properties, such as dissolution rate, shape (angles between facets and facet growth rates), melting point, etc. For this reason, polymorphism is of major importance in industrial manufacture of crystalline products.

Crystallization in nature



Snowflakes are a very well known example, where subtle differences in *crystal growth* conditions result in different geometries.



Crystallized honey

There are many examples of natural process that involve crystallization.

Geological time scale process examples include:

- Natural (mineral) crystal formation;
- Stalactite/stalagmite, rings formation.

Usual time scale process examples include:

- Snow flakes formation;
- Honey crystallization (nearly all types of honey crystallize).

Artificial methods

For crystallization to occur from a solution it must be supersaturated. This means that the solution has to contain more solute entities (molecules or ions) dissolved than it would contain under the equilibrium (saturated solution). This can be achieved by various methods, with (1) solution cooling, (2) addition of a second solvent to reduce the solubility of the solute (technique known as antisolvent or drown-out), (3) chemical reaction and (4) change in pH being the most common methods used in industrial practice. Other methods, such as solvent evaporation, can also be used. The spherical crystallization has some advantages (flowability and bioavailability) for the formulation of pharmaceutical drugs.

Applications

There are two major groups of applications for the *artificial crystallization* process: *crystal production* and purification.

Crystal production

From a material industry perspective:

- *Macroscopic crystal* production: for supply the demand of natural-like crystals with methods that "accelerate time-scale" for massive production and/or perfection.
    - *Ionic crystal* production;
    - *Covalent crystal* production.
- *Tiny size crystal*s:
    - *Powder, sand and smaller sizes*: using methods for powder and controlled (nanotechnology fruits) forms.
        - *Mass-production*: on chemical industry, like salt-powder production.
        - *Sample production*: small production of tiny crystals for material characterization. Controlled recrystallization is an important method to supply unusual crystals, that are needed to reveal the molecular structure and nuclear forces inside a typical molecule of a crystal. Many techniques, like X-ray crystallography and NMR spectroscopy, are widely used in chemistry and biochemistry to determine the structures of an immense variety of molecules, including inorganic compounds and bio-macromolecules.
    - Thin film production.

Massive production examples:

- "Powder salt for food" industry;
- Silicon crystal wafer production.
- Production of sucrose from sugar beet, where the sucrose is crystallized out from an aqueous solution.

Purification

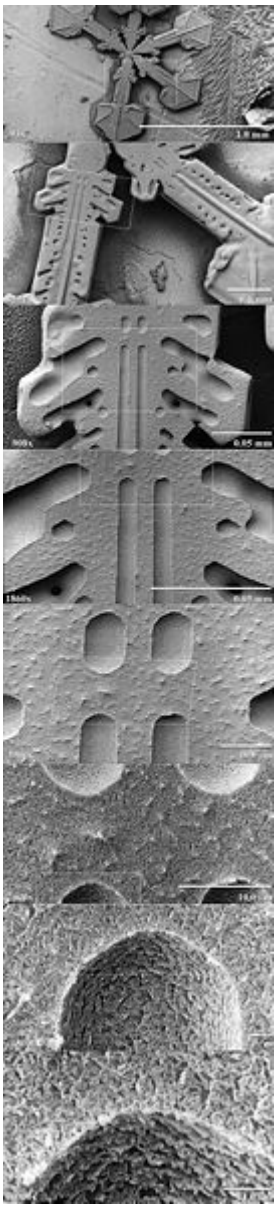
Used to improve (obtaining very pure substance) and/or verify their purity.

Crystallization separates a product from a liquid feedstream, often in extremely pure form, by cooling the feedstream or adding precipitants which lower the solubility of the desired product so that it forms crystals.

Well formed crystals are expected to be pure because each molecule or ion must fit perfectly into the lattice as it leaves the solution. Impurities would normally not fit as well in the lattice, and thus remain in solution preferentially. Hence, molecular recognition is the principle of purification in crystallization. However, there are instances when impurities incorporate into the lattice, hence, decreasing the level of purity of the final crystal product. Also, in some cases, the solvent may incorporate into the lattice

forming a *solvate*. In addition, the solvent may be 'trapped' (in liquid state) within the crystal formed, and this phenomenon is known as *inclusion*.

Thermodynamic view



Low-temperature SEM magnification series for a snow crystal. The crystals are captured, stored, and sputter coated with platinum at cryo-temperatures for imaging.

The nature of a crystallization process is governed by both thermodynamic and kinetic factors, which can make it highly variable and difficult to control. Factors such as impurity level, mixing regime, vessel design, and cooling profile can have a major impact on the size, number, and shape of crystals produced.

Now put yourself in the place of a molecule within a pure and *perfect crystal*, being heated by an external source. At some sharply defined temperature, a bell rings, you must leave your neighbours, and the complicated architecture of the crystal collapses to that of

a liquid. Textbook thermodynamics says that melting occurs because the entropy, S, gain in your system by spatial randomization of the molecules has overcome the enthalpy, H, loss due to breaking the crystal packing forces:

$$T(S_{liquid} - S_{solid}) > H_{liquid} - H_{solid}$$

$$G_{liquid} < G_{solid}$$

This rule suffers no exceptions when the temperature is rising. By the same token, on cooling the melt, at the very same temperature the bell should ring again, and molecules should click back into the very same crystalline form. The entropy decrease due to the ordering of molecules within the system is overcompensated by the thermal randomization of the surroundings, due to the release of the heat of fusion; the entropy of the universe increases.

But liquids that behave in this way on cooling are the exception rather than the rule; in spite of the second principle of thermodynamics, crystallization usually occurs at lower temperatures (supercooling). This can only mean that a crystal is more easily destroyed than it is formed. Similarly, it is usually much easier to dissolve a perfect crystal in a solvent than to grow again a good crystal from the resulting solution. The nucleation and growth of a crystal are under kinetic, rather than thermodynamic, control.

Equipment for crystallization

1. *Tank crystallizers*. Tank crystallization is an old method still used in some specialized cases. Saturated solutions, in tank crystallization, are allowed to cool in open tanks. After a period of time the mother liquid is drained and the crystals removed. Nucleation and size of crystals are difficult to control. Typically, labor costs are very high.
2. *Scraped surface crystallizers*. One type of scraped surface crystallizer is the Swenson-Walker crystallizer, which consists of an open trough 0.6 m wide with a semicircular bottom having a cooling jacket outside. A slow-speed spiral agitator rotates and suspends the growing crystals on turning. The blades pass close to the wall and break off any deposits of crystals on the cooled wall. The product generally has a somewhat wide crystal-size distribution.
3. *Double-pipe scraped surface crystallizer*. Also called a *votator*, this type of crystallizer is used in crystallizing ice cream and plasticizing margarine. Cooling water passes in the annular space. An internal agitator is fitted with spring-loaded scrapers that wipe the wall and provide good heat-transfer coefficients.
4. *Circulating-liquid evaporator-crystallizer*. Also called *Oslo crystallizer*. Here supersaturation is reached by evaporation. The circulating liquid is drawn by the screw pump down inside the tube side of the condensing stream heater. The heated liquid then flows into the vapor space, where flash evaporation occurs, giving some supersaturation.The vapor leaving is condensed. The supersaturated liquid flows down the downflow tube and then up through the bed of fluidized and agitated crystals, which are growing in size. The leaving saturated liquid then goes back as a recycle stream to the heater, where it is joined by the entering fluid. The larger crystals settle out and slurry of crystals and mother liquid is withdrawn as a product.

5. *Circulating-magma vacuum crystallizer*. The magma or suspension of crystals is circulated out of the main body through a circulating pipe by a screw pump. The magma flows though a heater, where its temperature is raised 2-6 K. The heated liquor then mixes with body slurry and boiling occurs at the liquid surface. This causes supersaturation in the swirling liquid near the surface, which deposits in the swirling suspended crystals until they leave again via the circulating pipe. The vapors leave through the top. A steam-jet ejector provides vacuum.
6. *Continuous oscillatory baffled crystallizer* (*COBC*). The COBC is a tubular baffled crystallizer that offers plug flow under laminar flow conditions (low flow rates) with superior heat transfer coefficient, allowing controlled cooling profiles, e.g. linear, parabolic, discontinued, step-wise or any type, to be achieved. This gives much better control over crystal size, morphology and consistent crystal products.

History

Crystallization is one of the pristine unit processes. It may be assumed that our ancestors used sodium chloride found in crevices of the surface rocks after drying caused by the sun: this process is still in use in modern solar ponds.

Other crystallization processes, for example sucrose production (this is the crystalline product with the largest world production, followed by sodium chloride), or in pigment manufacturing, were used in ancient times. These substances were sometimes produced by crystallizing the solutes of some more or less natural brine.

In more recent times, the fast expansion of the chemical industry has required a thorough study of the dynamics of crystallization, and this unit operation is now used in many industrial manufacturing areas: table salt, sugar, sodium sulfate, urea, just to name a few, are produced by crystallization from solutions.

Crystallizer technology has progressed alongside with the new processes. Once simple tanks in which, through cooling, evaporation or maybe through pH variation a crystal was obtained, nowadays continuous machines ensure a remarkable consistency in the product characteristics. Among the first models of modern crystallizers were probably the *calandria* type, being today the standard crystallizer for sucrose, and the *Oslo*, named after the Norwegian capital, since it was developed to produce salt in a climate not particularly fit for solar ponds, salt being widely used in Norway in stockfish production. The Oslo type was probably the first crystallizer designed specifically for the control of crystal growth.

Crystallization dynamics

As mentioned above, a crystal is formed following a well-defined pattern, or structure, dictated by forces acting at the molecular level. As a consequence, during its formation process the crystal is in an environment where the solute concentration reaches a certain critical value, before changing status. Solid formation, impossible below the solubility threshold at the given temperature and pressure conditions, may then take place at a concentration higher than the theoretical solubility level. The difference between the actual value of the solute concentration at the crystallization limit and the theoretical

(static) solubility threshold is called supersaturation and is a fundamental factor in crystallization dynamics. Supersaturation is the driving force for both the initial nucleation step and the following crystal growth, both of which could not occur in saturated or undersaturated conditions.

Nucleation

Nucleation is the initiation of a phase change in a small region, such as the formation of a solid crystal from a liquid solution. It is a consequence of rapid local fluctuations on a molecular scale in a homogeneous phase that is in a state of metastable equilibrium. Total nucleation is the sum effect of two categories of nucleation - primary and secondary.

Primary nucleation

Primary nucleation is the initial formation of a crystal where there are no other crystals present or where, if there are crystals present in the system, they do not have any influence on the process. This can occur in two conditions. The first is homogeneous nucleation, which is nucleation that is not influenced in any way by solids. These solids include the walls of the crystallizer vessel and particles of any foreign substance. The second category, then, is heterogeneous nucleation. This occurs when solid particles of foreign substances cause an increase in the rate of nucleation that would otherwise not be seen without the existence of these foreign particles. Homogeneous nucleation rarely occurs in practice due to the high energy necessary to begin nucleation without a solid surface to catalyse the nucleation.

Primary nucleation (both homogeneous and heterogeneous) has been modelled with the following:

$$B = \frac{dN}{dt} = k_n(c - c^*)^n$$

- B is the number of nuclei formed per unit volume per unit time.
- N is the number of nuclei per unit volume.
- k_{np} is a rate constant.
- c is the instantaneous solute concentration.
- c^* is the solute concentration at saturation.
- $(c-c^*)$ is also known as supersaturation.
- n is an empirical exponent that can be as large as 10, but generally ranges between 3 and 4.

Secondary nucleation

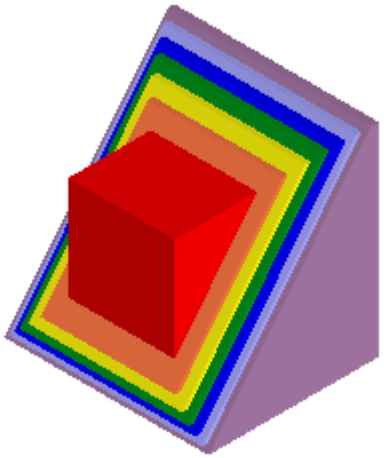
Secondary nucleation is the formation of nuclei attributable to the influence of the existing microscopic crystals in the magma. The first type of known secondary crystallization is attributable to fluid shear, the other due to collisions between already existing crystals with either a solid surface of the crystallizer or with other crystals themselves. Fluid shear nucleation occurs when liquid travels across a Crystal at a high speed, sweeping away nuclei that would otherwise be incorporated into a Crystal, causing the swept-away nuclei to become new crystals. Contact nucleation has been found to be the most effective and common method for nucleation. The benefits include the following

- Low kinetic order and rate-proportional to supersaturation, allowing easy control without unstable operation.
- Occurs at low supersaturation, where growth rate is optimum for good quality.
- Low necessary energy at which crystals strike avoids the breaking of existing crystals into new crystals.
- The quantitative fundamentals have already been isolated and are being incorporated into practice.

The following model, although somewhat simplified, is often used to model secondary nucleation:

$$B = \frac{dN}{dt} = k_1 M_T^j (c - c^*)^b$$

- k_1 is a rate constant.
- M_T is the suspension density.
- j is an empirical exponent that can range up to 1.5, but is generally 1.
- b is an empirical exponent that can range up to 5, but is generally 2.



Crystal growth

Crystal growth

Once the first small crystal, the nucleus, forms it acts as a convergence point (if unstable due to supersaturation) for molecules of solute touching - or adjacent to - the crystal so that it increases its own dimension in successive layers. The pattern of growth resembles the rings of an onion, as shown in the picture, where each colour indicates the same mass of solute; this mass creates increasingly thin layers due to the increasing surface area of the growing crystal. The supersaturated solute mass the original nucleus may *capture* in a time unit is called the *growth rate* expressed in kg/(m^2*h), and is a constant specific to the process. Growth rate is influenced by several physical factors, such as surface tension of solution, pressure, temperature, relative crystal velocity in the solution, Reynolds number, and so forth.

The main values to control are therefore:

- Supersaturation value, as an index of the quantity of solute available for the growth of the crystal;
- Total crystal surface in unit fluid mass, as an index of the capability of the solute to fix onto the crystal;
- Retention time, as an index of the probability of a molecule of solute to come into contact with an existing crystal;
- Flow pattern, again as an index of the probability of a molecule of solute to come into contact with an existing crystal (higher in laminar flow, lower in turbulent flow, but the reverse applies to the probability of contact).

The first value is a consequence of the physical characteristics of the solution, while the others define a difference between a well- and poorly designed crystallizer.

Crystal size distribution

The appearance and size range of a crystalline product is extremely important in crystallization. If further processing of the crystals is desired, large crystals with uniform size are important for washing, filtering, transportation, and storage. The importance lies in the fact that large crystals are easier to filter out of a solution than small crystals. Also, larger crystals have a smaller surface area to volume ratio, leading to a higher purity. This higher purity is due to less retention of mother liquor which contains impurities, and a smaller loss of yield when the crystals are washed to remove the mother liquor. The theoretical crystal size distribution can be estimated as a function of operating conditions with a fairly complicated mathematical process called population balance theory (using population balance equations).

Main crystallization processes

The main factors influencing solubility are, as we saw above:

- Concentration
- Temperature

So we may identify two main families of crystallization processes:

- Cooling crystallization
- Evaporative crystallization

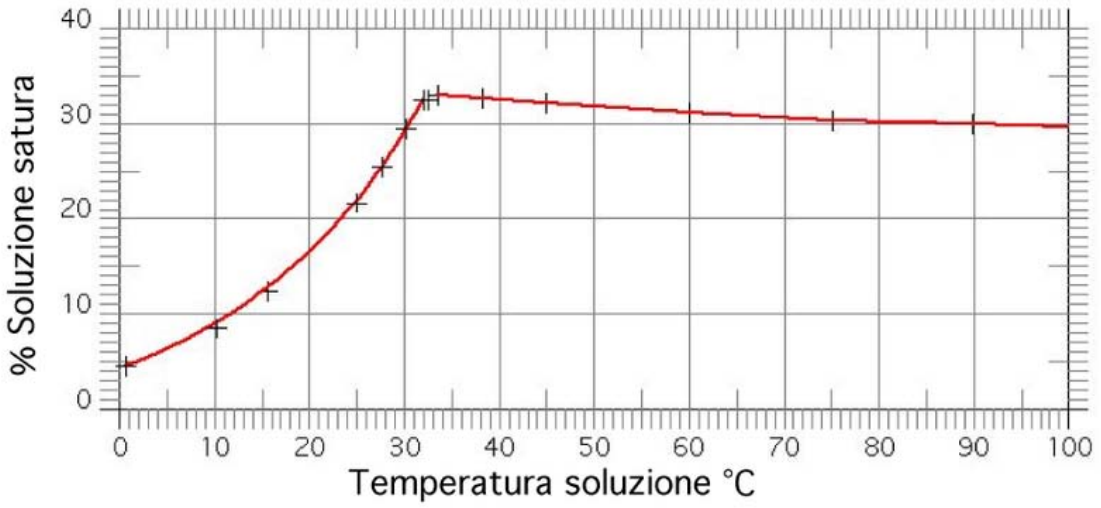
This division is not really clear-cut, since hybrid systems exist, where cooling is performed through evaporation, thus obtaining at the same time a concentration of the solution.

A crystallization process often referred to in chemical engineering is the Fractional crystallization. This is not a different process, rather a special application of one (or both) of the above.

Cooling crystallization

Application

Most chemical compounds, dissolved in most solvents, show the so-called *direct* solubility that is, the solubility threshold increases with temperature.



Solubility of the system Na_2SO_4 - H_2O

So, whenever the conditions are favourable, crystal formation results from simply cooling the solution. Here *cooling* is a relative term: austenite crystals in a steel form well above 1000 °C. An example of this crystallization process is the production of Glauber's salt, a crystalline form of sodium sulphate. In the picture, where equilibrium temperature is on the x-axis and equilibrium concentration (as mass percent of solute in saturated solution) in y-axis, it is clear that sulphate solubility quickly decreases below 32.5 °C. Assuming a saturated solution at 30 °C, by cooling it to 0 °C (note that this is possible thanks to the freezing-point depression), the precipitation of a mass of sulphate occurs corresponding to the change in solubility from 29% (equilibrium value at 30°C) to approximately 4.5% (at 0°C) - actually a larger crystal mass is precipitated, since sulphate entrains hydration water, and this has the side effect of increasing the final concentration.

There are of course limitation in the use of cooling crystallization:

- Many solutes precipitate in hydrate form at low temperatures: in the previous example this is acceptable, and even useful, but it may be detrimental when, for example, the mass of water of hydration to reach a stable hydrate crystallization form is more than the available water: a single block of hydrate solute will be formed - this occurs in the case of calcium chloride);
- Maximum supersaturation will take place in the coldest points. These may be the heat exchanger tubes which are sensitive to scaling, and heat exchange may be greatly reduced or discontinued;
- A decrease in temperature usually implies an increase of the viscosity of a solution. Too high a viscosity may give hydraulic problems, and the laminar flow thus created may affect the crystallization dynamics.

- It is of course not applicable to compounds having *reverse* solubility, a term to indicate that solubility increases with temperature decrease (an example occurs with sodium sulphate where solubility is reversed above 32.5 °C).

Cooling crystallizers

The simplest cooling crystallizers are tanks provided with a mixer for internal circulation, where temperature decrease is obtained by heat exchange with an intermediate fluid circulating in a jacket. These simple machines are used in batch processes, as in processing of pharmaceuticals and are prone to scaling. Batch processes normally provide a relatively variable quality of product along the batch.

The *Swenson-Walker* crystallizer is a model, specifically conceived by Swenson Co. around 1920, having a semicylindric horizontal hollow trough in which a hollow screw conveyor or some hollow discs, in which a refrigerating fluid is circulated, plunge during rotation on a longitudinal axis. The refrigerating fluid is sometimes also circulated in a jacket around the trough. Crystals precipitate on the cold surfaces of the screw/discs, from which they are removed by scrapers and settle on the bottom of the trough. The screw, if provided, pushes the slurry towards a discharge port.

A common practice is to cool the solutions by flash evaporation: when a liquid at a given T_0 temperature is transferred in a chamber at a pressure P_1 such that the liquid saturation temperature T_1 at P_1 is lower than T_0, the liquid will release heat according to the temperature difference and a quantity of solvent, whose total latent heat of vaporization equals the difference in enthalpy. In simple words, the liquid is cooled by evaporating a part of it.

Evaporative crystallization

Another option is to obtain, at an approximately constant temperature, the precipitation of the crystals by increasing the solute concentration above the solubility threshold. To obtain this, the solute/solvent mass ratio is increased using the technique of evaporation. This process is of course insensitive to change in temperature (as long as hydration state remains unchanged).

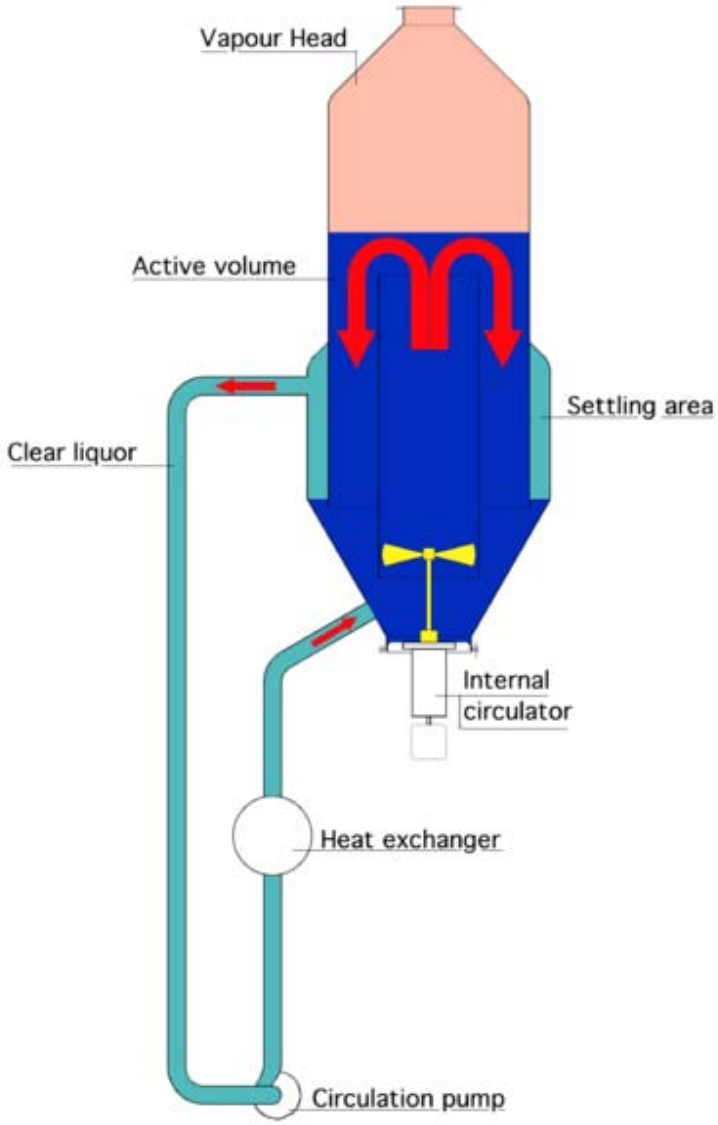
All considerations on control of crystallization parameters are the same as for the cooling models.

Evaporative crystallizers

Most industrial crystallizers are of the evaporative type, such as the very large sodium chloride and sucrose units, whose production accounts for more than 50% of the total world production of crystals. The most common type is the *forced circulation* (FC) model. A pumping device (a pump or an axial flow mixer) keeps the crystal slurry in homogeneous suspension throughout the tank, including the exchange surfaces; by controlling pump flow, control of the contact time of the crystal mass with the supersaturated solution is achieved, together with reasonable velocities at the exchange surfaces. The Oslo, mentioned above, is a refining of the evaporative forced circulation crystallizer, now equipped with a large crystals settling zone to increase the retention time (usually low in the FC) and to roughly separate heavy slurry zones from clear liquid.

The DTB crystallizer

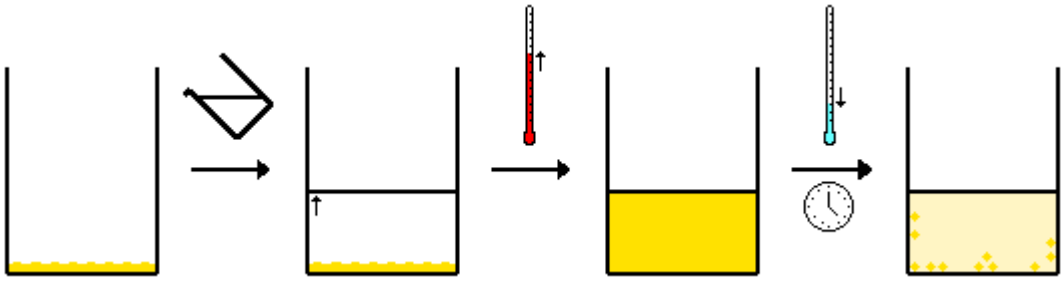
DTB Crystallizer



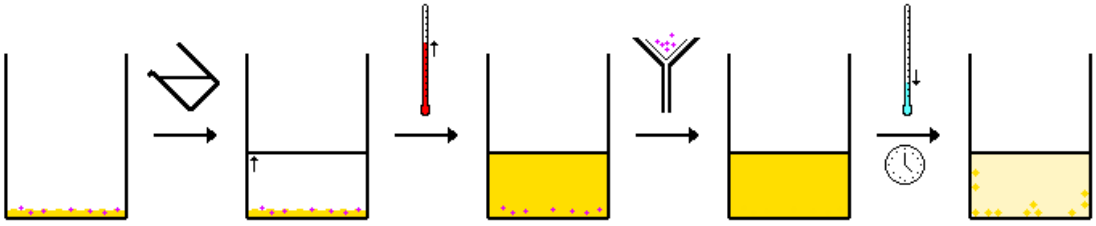
Schematic of DTB

Whichever the form of the crystallizer, to achieve an effective process control it is important to control the retention time and the crystal mass, to obtain the optimum conditions in terms of crystal specific surface and the fastest possible growth. This is achieved by a separation - to put it simply - of the crystals from the liquid mass, in order to manage the two flows in a different way. The practical way is to perform a gravity settling to be able to extract (and possibly recycle separately) the (almost) clear liquid, while managing the mass flow around the crystallizer to obtain a precise slurry density elsewhere. A typical example is the DTB (*Draft Tube and Baffle*) crystallizer, an idea of Richard Chisum Bennett (a Swenson engineer and later President of Swenson) at the end of the 1950s. The DTB crystallizer has an internal circulator, typically an axial flow mixer - yellow - pushing upwards in a draft tube while outside the crystallizer there is a settling area in an annulus; in it the exhaust solution moves upwards at a very low velocity, so that large crystals settle - and return to the main circulation - while only the fines, below a given grain size are extracted and eventually destroyed by increasing or decreasing temperature, thus creating additional supersaturation. A quasi-perfect control of all parameters is achieved. This crystallizer, and the derivative models (Krystal, CSC, etc.) could be the ultimate solution if not for a major limitation in the evaporative capacity, due to the limited diameter of the vapour head and the relatively low external circulation not allowing large amounts of energy to be supplied to the system.

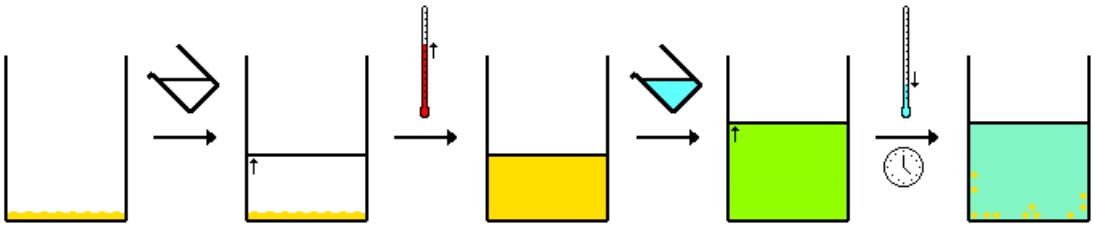
Solvent recrystallisation



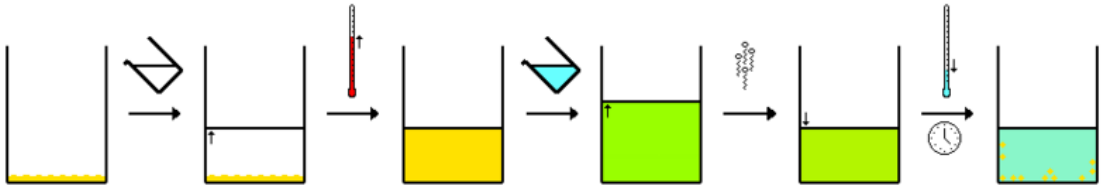
The process



Hot-filtration, 1 solvent

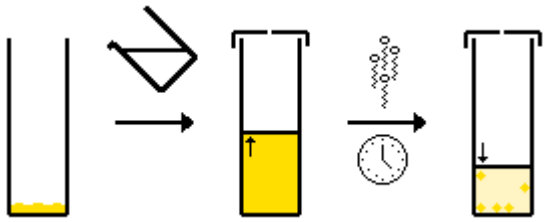


2 solvent

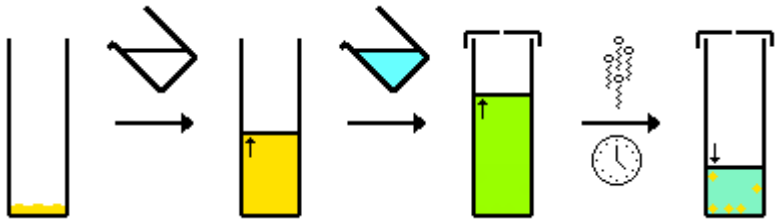


2 solvent, with evaporation

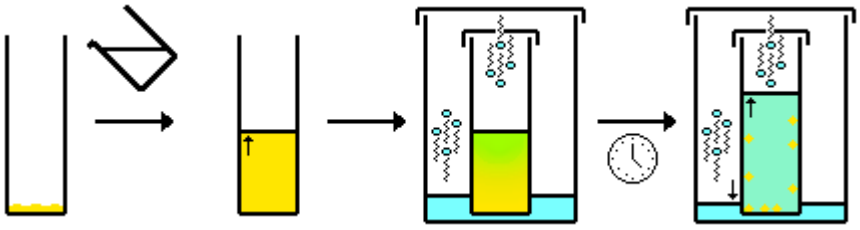
X-ray crystals



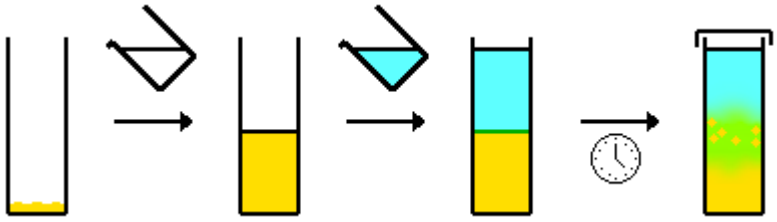
slow evaporation 1 solvent



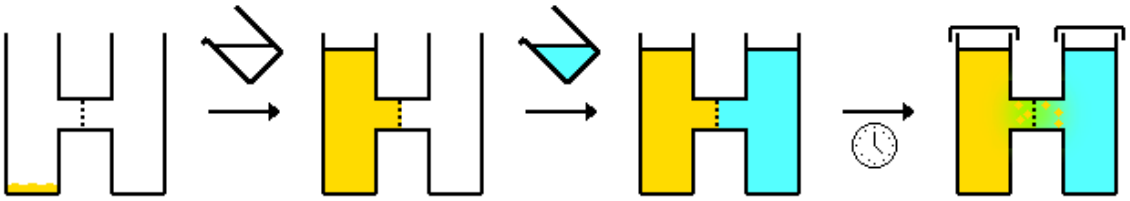
slow evaporation 2 solvent



slow gas diffusion 2 solvent



slow liquid diffusion



slow liquid diffusion - H Tube

Chapter 9

Catalytic Reforming

Catalytic reforming is a chemical process used to convert petroleum refinery naphthas, typically having low octane ratings, into high-octane liquid products called **reformates** which are components of high-octane gasoline (also known as petrol). Basically, the process re-arranges or re-structures the hydrocarbon molecules in the naphtha feedstocks as well as breaking some of the molecules into smaller molecules. The overall effect is that the product reformate contains hydrocarbons with more complex molecular shapes having higher octane values than the hydrocarbons in the naphtha feedstock. In so doing, the process separates hydrogen atoms from the hydrocarbon molecules and produces very significant amounts of byproduct hydrogen gas for use in a number of the other processes involved in a modern petroleum refinery. Other byproducts are small amounts of methane, ethane, propane and butanes.

This process is quite different from and not to be confused with the catalytic steam reforming process used industrially to produce various products such as hydrogen, ammonia and methanol from natural gas, naphtha or other petroleum-derived feedstocks. Nor is this process to be confused with various other catalytic reforming processes that use methanol or biomass-derived feedstocks to produce hydrogen for fuel cells or other uses.

History

In the 1940s, Vladimir Haensel, a research chemist working for Universal Oil Products (UOP), developed a catalytic reforming process using a catalyst containing platinum. Haensel's process was subsequently commercialized by UOP in 1949 for producing a high octane gasoline from low octane naphthas and the UOP process become known as the Platforming process. The first Platforming unit was built in 1949 at the refinery of the Old Dutch Refining Company in Muskegon, Michigan.

In the years since then, many other versions of the process have been developed by some of the major oil companies and other organizations. Today, the large majority of gasoline produced worldwide is derived from the catalytic reforming process.

To name a few of the other catalytic reforming versions that were developed, all of which utilized a platinum and/or a rhenium catalyst:

- Rheniforming: Developed by Chevron Oil Company.
- Powerforming: Developed by Esso Oil Company, now known as ExxonMobil.
- Magnaforming: Developed by Englehard Catalyst Company and Atlantic Richfield Oil Company.
- Ultraforming: Developed by Standard Oil of Indiana, now a part of the British Petroleum Company.
- Houdriforming: Developed by the Houdry Process Corporation.
- CCR Platforming: A Platforming version, designed for continuous catalyst regeneration, developed by UOP.
- Octanizing: A catalytic reforming version developed by Axens, a subsidiary of Institut francais du petrole (IFP), designed for continuous catalyst regeneration.

Chemistry

Before describing the reaction chemistry of the catalytic reforming process as used in petroleum refineries, the typical naphthas used as catalytic reforming feedstocks will be discussed.

Typical naphtha feedstocks

A petroleum refinery includes many unit operations and unit processes. The first unit operation in a refinery is the continuous distillation of the petroleum crude oil being refined. The overhead liquid distillate is called naphtha and will become a major component of the refinery's gasoline (petrol) product after it is further processed through a catalytic hydrodesulfurizer to remove sulfur-containing hydrocarbons and a catalytic reformer to reform its hydrocarbon molecules into more complex molecules with a higher octane rating value. The naphtha is a mixture of very many different hydrocarbon compounds. It has an initial boiling point of about 35 °C and a final boiling point of about 200 °C, and it contains paraffin, naphthene (cyclic paraffins) and aromatic hydrocarbons ranging from those containing 4 carbon atoms to those containing about 10 or 11 carbon atoms.

The naphtha from the crude oil distillation is often further distilled to produce a "light" naphtha containing most (but not all) of the hydrocarbons with 6 or less carbon atoms and a "heavy" naphtha containing most (but not all) of the hydrocarbons with more than 6 carbon atoms. The heavy naphtha has an initial boiling point of about 140 to 150 °C and a final boiling point of about 190 to 205 °C. The naphthas derived from the distillation of crude oils are referred to as "straight-run" naphthas.

It is the straight-run heavy naphtha that is usually processed in a catalytic reformer because the light naphtha has molecules with 6 or less carbon atoms which, when reformed, tend to crack into butane and lower molecular weight hydrocarbons which are not useful as high-octane gasoline blending components. Also, the molecules with 6 carbon atoms tend to form aromatics which is undesirable because governmental environmental regulations in a number of countries limit the amount of aromatics (most particularly benzene) that gasoline may contain.

It should be noted that there are a great many petroleum crude oil sources worldwide and each crude oil has its own unique composition or "assay". Also, not all refineries process the same crude oils and each refinery produces its own straight-run naphthas with their own unique initial and final boiling points. In other words, naphtha is a generic term rather than a specific term.

The table just below lists some fairly typical straight-run heavy naphtha feedstocks, available for catalytic reforming, derived from various crude oils. It can be seen that they differ significantly in their content of paraffins, naphthenes and aromatics:

Typical Heavy Naphtha Feedstocks

Crude oil name ⇒ **Location ⇒**	**Barrow Island** **Australia**	**Mutineer-Exeter** **Australia**	**CPC Blend** **Kazakhstan**	**Draugen** **North Sea**
Initial boiling point, °C	149	140	149	150
Final boiling point, °C	204	190	204	180
Paraffins, liquid volume %	46	62	57	38
Naphthenes, liquid volume %	42	32	27	45
Aromatics, liquid volume %	12	6	16	17

Some refinery naphthas include olefinic hydrocarbons, such as naphthas derived from the fluid catalytic cracking and coking processes used in many refineries. Some refineries may also desulfurize and catalytically reform those naphthas. However, for the most part, catalytic reforming is mainly used on the straight-run heavy naphthas, such as those in the above table, derived from the distillation of crude oils.

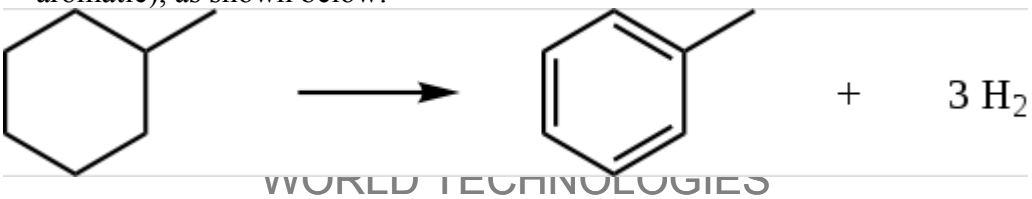
The reaction chemistry

There are a good many chemical reactions that occur in the catalytic reforming process, all of which occur in the presence of a catalyst and a high partial pressure of hydrogen. Depending upon the type or version of catalytic reforming used as well as the desired reaction severity, the reaction conditions range from temperatures of about 495 to 525 °C and from pressures of about 5 to 45 atm.

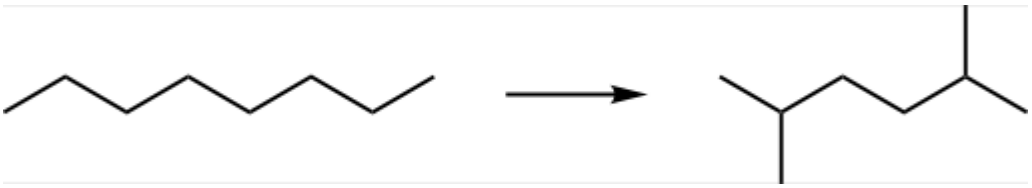
The commonly used catalytic reforming catalysts contain noble metals such as platinum and/or rhenium, which are very susceptible to poisoning by sulfur and nitrogen compounds. Therefore, the naphtha feedstock to a catalytic reformer is always pre-processed in a hydrodesulfurization unit which removes both the sulfur and the nitrogen compounds.

The four major catalytic reforming reactions are:

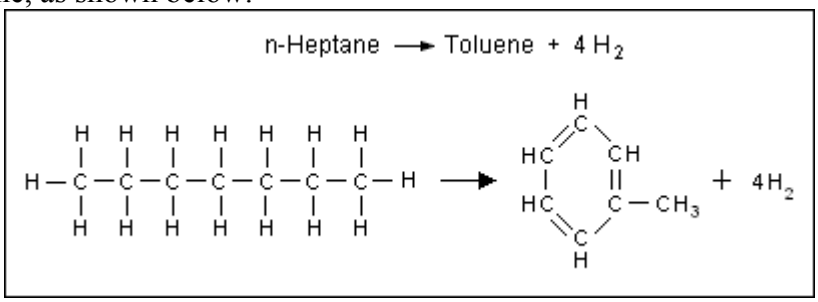
1: The dehydrogenation of naphthenes to convert them into aromatics as exemplified in the conversion methylcyclohexane (a naphthene) to toluene (an aromatic), as shown below:



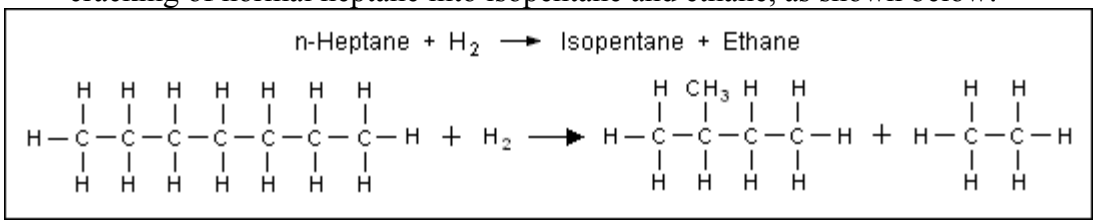
2: The isomerization of normal paraffins to isoparaffins as exemplified in the conversion of normal octane to 2,5-Dimethylhexane (an isoparaffin), as shown below:



3: The dehydrogenation and aromatization of paraffins to aromatics (commonly called dehydrocyclization) as exemplified in the conversion of normal heptane to toluene, as shown below:



4: The hydrocracking of paraffins into smaller molecules as exemplified by the cracking of normal heptane into isopentane and ethane, as shown below:



The hydrocracking of paraffins is the only one of the above four major reforming reactions that consumes hydrogen. The isomerization of normal paraffins does not consume or produce hydrogen. However, both the dehydrogenation of naphthenes and the dehydrocyclization of paraffins produce hydrogen. The overall net production of hydrogen in the catalytic reforming of petroleum naphthas ranges from about 50 to 200 cubic meters of hydrogen gas (at 0 °C and 1 atm) per cubic meter of liquid naphtha feedstock. In the United States customary units, that is equivalent to 300 to 1200 cubic feet of hydrogen gas (at 60 °F and 1 atm) per barrel of liquid naphtha feedstock. In many petroleum refineries, the net hydrogen produced in catalytic reforming supplies a significant part of the hydrogen used elsewhere in the refinery (for example, in hydrodesulfurization processes). The hydrogen is also necessary in order to hydrogenolyze any polymers that form on the catalyst.

Process description

The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst, and all of the catalyst is regenerated *in situ* during routine catalyst regeneration shutdowns which occur approximately once each 6 to 24 months. Such a unit is referred to as a semi-regenerative catalytic reformer (SRR).

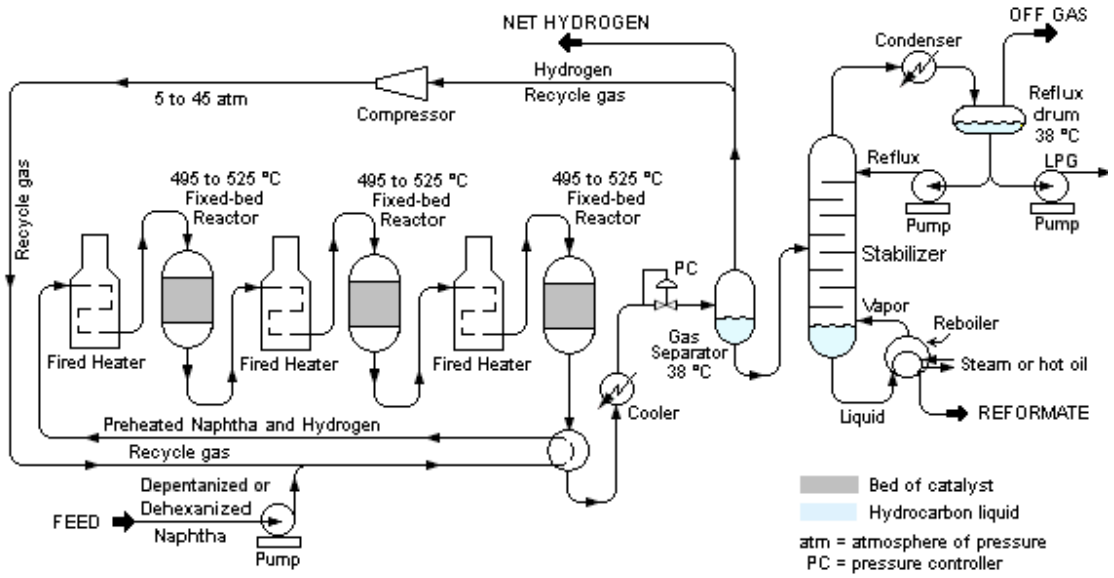
Some catalytic reforming units have an extra *spare* or *swing* reactor and each reactor can be individually isolated so that any one reactor can be undergoing in situ regeneration

while the other reactors are in operation. When that reactor is regenerated, it replaces another reactor which, in turn, is isolated so that it can then be regenerated. Such units, referred to as *cyclic* catalytic reformers, are not very common. Cyclic catalytic reformers serve to extend the period between required shutdowns.

The latest and most modern type of catalytic reformers are called continuous catalyst regeneration reformers (CCR). Such units are characterized by continuous in-situ regeneration of part of the catalyst in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors. As of 2006, two CCR versions available: UOP's CCR Platformer process and Axen's Octanizing process. The installation and use of CCR units is rapidly increasing.

Many of the earliest catalytic reforming units (in the 1950s and 1960's) were non-regenerative in that they did not perform in situ catalyst regeneration. Instead, when needed, the aged catalyst was replaced by fresh catalyst and the aged catalyst was shipped to catalyst manufacturer's to be either regenerated or to recover the platinum content of the aged catalyst. Very few, if any, catalytic reformers currently in operation are non-regenerative.

The process flow diagram below depicts a typical semi-regenerative catalytic reforming unit.



Schematic diagram of a typical semi-regenerative catalytic reformer unit in a petroleum refinery

The liquid feed (at the bottom left in the diagram) is pumped up to the reaction pressure (5 to 45 atm) and is joined by a stream of hydrogen-rich recycle gas. The resulting liquid-gas mixture is preheated by flowing through a heat exchanger. The preheated feed mixture is then totally vaporized and heated to the reaction temperature (495 to 520 °C) before the vaporized reactants enter the first reactor. As the vaporized reactants flow through the fixed bed of catalyst in the reactor, the major reaction is the dehydrogenation of naphthenes to aromatics (as described earlier herein) which is highly endothermic and results in a large temperature decrease between the inlet and outlet of the reactor. To maintain the required reaction temperature and the rate of reaction, the vaporized stream

is reheated in the second fired heater before it flows through the second reactor. The temperature again decreases across the second reactor and the vaporized stream must again be reheated in the third fired heater before it flows through the third reactor. As the vaporized stream proceeds through the three reactors, the reaction rates decrease and the reactors therefore become larger. At the same time, the amount of reheat required between the reactors becomes smaller. Usually, three reactors are all that is required to provide the desired performance of the catalytic reforming unit.

Some installations use three separate fired heaters as shown in the schematic diagram and some installations use a single fired heater with three separate heating coils.

The hot reaction products from the third reactor are partially cooled by flowing through the heat exchanger where the feed to the first reactor is preheated and then flow through a water-cooled heat exchanger before flowing through the pressure controller (PC) into the gas separator.

Most of the hydrogen-rich gas from the gas separator vessel returns to the suction of the recycle hydrogen gas compressor and the net production of hydrogen-rich gas from the reforming reactions is exported for use in the other refinery processes that consume hydrogen (such as hydrodesulfurization units and/or a hydrocracker unit).

The liquid from the gas separator vessel is routed into a fractionating column commonly called a *stabilizer*. The overhead offgas product from the stabilizer contains the byproduct methane, ethane, propane and butane gases produced by the hydrocracking reactions as explained in the above discussion of the reaction chemistry of a catalytic reformer, and it may also contain some small amount of hydrogen. That offgas is routed to the refinery's central gas processing plant for removal and recovery of propane and butane. The residual gas after such processing becomes part of the refinery's fuel gas system.

The bottoms product from the stabilizer is the high-octane liquid reformate that will become a component of the refinery's product gasoline.

Catalysts and mechanisms

Most catalytic reforming catalysts contain platinum or rhenium on a silica or silica-alumina support base, and some contain both platinum and rhenium. Fresh catalyst is chlorided (chlorinated) prior to use.

The noble metals (platinum and rhenium) are considered to be catalytic sites for the dehydrogenation reactions and the chlorinated alumina provides the acid sites needed for isomerization, cyclization and hydrocracking reactions.

The activity (i.e., effectiveness) of the catalyst in a semi-regenerative catalytic reformer is reduced over time during operation by carbonaceous coke deposition and chloride loss. The activity of the catalyst can be periodically regenerated or restored by in situ high temperature oxidation of the coke followed by chlorination. As stated earlier herein, semi-regenerative catalytic reformers are regenerated about once per 6 to 24 months.

Normally, the catalyst can be regenerated perhaps 3 or 4 times before it must be returned to the manufacturer for reclamation of the valuable platinum and/or rhenium content.

Chapter 10

Chemical Reaction

A thermite reaction using ferric oxide

A **chemical reaction** is a process that leads to the transformation of one set of chemical substances to another. Chemical reactions can be either spontaneous, requiring no input of energy, or non-spontaneous, typically following the input of some type of energy, viz. heat, light or electricity. Classically, chemical reactions encompass changes that strictly

involve the motion of electrons in the forming and breaking of chemical bonds, although the general concept of a chemical reaction, in particular the notion of a chemical equation, is applicable to transformations of elementary particles, as well as nuclear reactions.

The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change, and they yield one or more products, which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations, which graphically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Different chemical reactions are used in combination in chemical synthesis in order to obtain a desired product. In biochemistry, series of chemical reactions catalyzed by enzymes form metabolic pathways, by which syntheses and decompositions impossible under ordinary conditions are performed within a cell.

History

Antoine Lavoisier developed the theory of combustion as a chemical reaction with oxygen

Chemical reactions such as combustion in the fire, fermentation and the reduction of ores to metals were known since antiquity. Initial theories of transformation of materials were developed by Greek philosophers, such as the Four-Element Theory of Empedocles stating that any substance is composed of the four basic elements – fire, water, air and earth. In the Middle Ages, chemical transformations were studied by Alchemist. They

attempted, in particular, to convert lead into gold, for which purpose they used reactions of lead and lead-copper alloys with sulfur.

The production of chemical substances that do not normally occur in nature has long been tried, such as the synthesis of sulfuric and nitric acids attributed to the controversial alchemist Jābir ibn Hayyān. The process involved heating of sulfate and nitrate minerals such as copper sulfate, alum and saltpeter. In the 17th century, Johann Rudolph Glauber produced hydrochloric acid and sodium sulfate by reacting sulfuric acid and sodium chloride. With the development of the lead chamber process in 1746 and the Leblanc process, allowing large-scale production of sulfuric acid and sodium carbonate, respectively, chemical reactions became implemented into the industry. Further optimization of sulfuric acid technology resulted in the contact process in 1880s, and the Haber process was developed in 1909–1910 for ammonia synthesis.

From the 16th century, researchers including Jan Baptist van Helmont, Robert Boyle and Isaac Newton tried to establish theories of the experimentally observed chemical transformations. The phlogiston theory was proposed in 1667 by Johann Joachim Becher. It postulated the existence of a fire-like element called "phlogiston", which was contained within combustible bodies and released during combustion. This proved to be false in 1785 by Antoine Lavoisier who found the correct explanation of the combustion as reaction with oxygen from the air.

Joseph Louis Gay-Lussac recognized in 1808 that gases always react in a certain relationship with each other. Based on this idea and the atomic theory of John Dalton, Joseph Proust had developed the law of definite proportions, which later resulted in the concepts of stoichiometry and chemical equations.

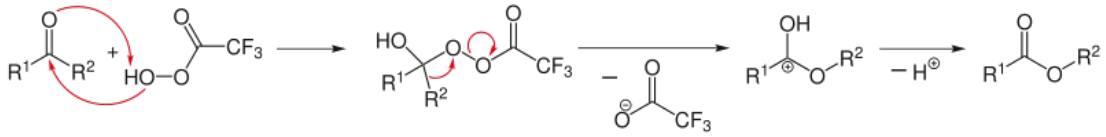
Regarding the organic chemistry, it was long believed that compounds obtained from living organisms were too complex to be obtained synthetically. According to the concept of vitalism, organic matter was endowed with a "vital force" and distinguished from inorganic materials. This separation was ended however by the synthesis of urea from inorganic precursors by Friedrich Wöhler in 1828. Other chemists who brought major contributions to organic chemistry include Alexander William Williamson with his synthesis of ethers and Christopher Kelk Ingold, who, among many discoveries, established the mechanisms of substitution reactions.

Equations

Chemical equations are used to graphically illustrate chemical reactions. They consist of chemical or structural formulas of the reactants on the left and those of the products on the right. They are separated by an arrow (→) which indicates the direction and type of the reaction. The tip of the arrow points in the direction in which the reaction proceeds. A double arrow (⇌) pointing in opposite directions is used for equilibrium reactions. Equations should be balanced according to the stoichiometry, the number of atoms of each species should be the same on both sides of the equation. This is achieved by scaling the number of involved molecules (*A, B, C* and *D* in a schematic example below) by the appropriate integers *a, b, c* and *d*.

$$\mathrm{a\ A + b\ B \longrightarrow c\ C + d\ D}$$

More complex reactions are represented by reaction schemes, which in addition to starting materials and products show important intermediates or transition states. Also, some relatively minor additions to the reaction can be indicated above the reaction arrow; examples of such additions are water, heat, illumination, a catalyst, etc. Similarly, some minor products can be placed below the arrow, often with a minus sign.

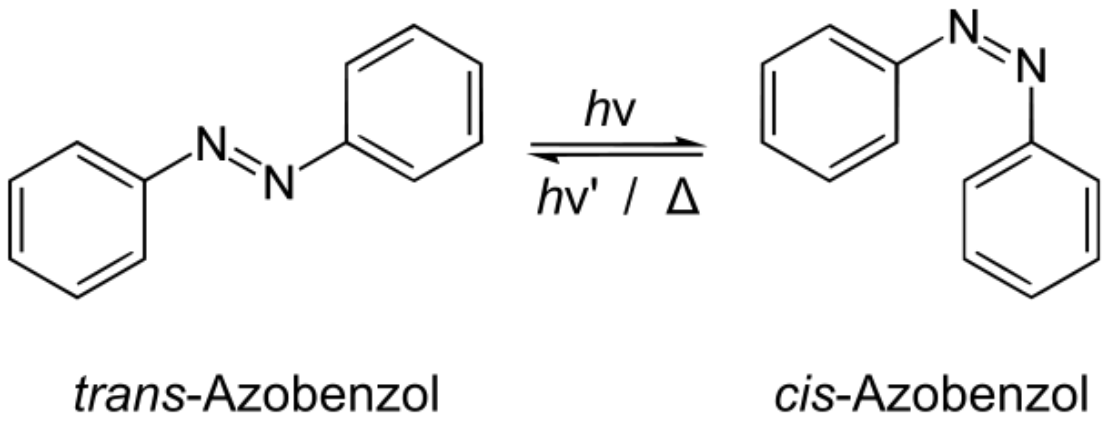


An example of organic reaction: oxidation of ketones to esters with peroxycarboxylic acid

Retrosynthetic analysis can be applied to design a complex synthesis reaction. Here the analysis starts from the products, for example by splitting selected chemical bonds, to arrive at plausible initial reagents. A special arrow (⇒) is used in retro reactions.

Elementary reactions

The elementary reaction is the smallest division into which a chemical reaction can be decomposed to, it has no intermediate products. Most experimentally observed reactions are built up from many elementary reactions that occur in parallel or sequentially. The actual sequence of the individual elementary reactions is known as reaction mechanism. An elementary reaction involves a few molecules, usually one or two, because of the low probability for several molecules to meet at a certain time.



Isomerization of azobenzene, induced by light (hν) or heat (Δ)

The most important elementary reactions are unimolecular and bimolecular reactions. Only one molecule is involved in a unimolecular reaction; it is transformed by an isomerization or a dissociation in one or more other molecules. Such reaction requires addition of energy in the form of heat or light. A typical example of a unimolecular reaction is the cis–trans isomerization, in which the cis-form of a compound converts to the trans-form or vice versa.

In a typical dissociation reaction, a bond in a molecule splits resulting in two molecular fragments. The splitting can be homolytic or heterolytic. In the first case, the bond is divided so that each product retains an electron and becomes a neutral radical. In the second case, both electrons of the chemical bond remain with one of the products, resulting in charged ions. Dissociation plays an important role in triggering chain reactions, such as hydrogen-oxygen or polymerization reactions.

$$\mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B}$$

Dissociation of a molecule AB into fragments A and B

For bimolecular reactions, two molecules collide and react with each other. Their merger is called chemical synthesis or an addition reaction.

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{AB}$$

Another possibility is that only a portion of one molecule is transferred to the other molecule. This type of reaction occurs, for example, in redox and acid-base reactions. In redox reactions, the transferred particle is an electron, whereas in acid-base reactions it is a proton. This type of reaction is also called metathesis.

$$\mathrm{HA} + \mathrm{B} \longrightarrow \mathrm{A} + \mathrm{HB}$$

for example

$$\mathrm{NaCl_{(aq)}} + \mathrm{AgNO_{3(aq)}} \rightarrow \mathrm{NaNO_{3(aq)}} + \mathrm{AgCl_{(s)}}$$

Chemical equilibrium

Most chemical reactions are reversible, that is they can and do run in both directions. The forward and reverse reactions are competing with each other and differ in reaction rates. These rates depend on the concentration and therefore change with time of the reaction: the reverse rate gradually increases and becomes equal to the rate of the forward reaction, establishing the so-called chemical equilibrium. The time to reach equilibrium depends on such parameters as temperature, pressure and the materials involved, and is determined by the minimum free energy. In equilibrium, the Gibbs free energy must be zero. The pressure dependence can be explained with the Le Chatelier's principle. For example, an increase in pressure due to decreasing volume causes the reaction to shift to the side with the fewer moles of gas.

The reaction yield stabilized at equilibrium, but can be increased by removing the product from the reaction mixture or increasing temperature or pressure. Change in the initial concentrations of the substances does not affect the equilibrium.

Thermodynamics

Chemical reactions are largely determined by the laws of thermodynamics. Reactions can proceed by themselves if they are exergonic, that is if they release energy. The associated free energy of the reaction is composed of two different thermodynamic quantities, enthalpy and entropy:

$$\Delta G = \Delta H - T \cdot \Delta S$$
G: free energy, H: enthalpy, T: temperature, S: entropy, Δ: difference

Reactions can be exothermic, where ΔH is negative and energy is released. Typical examples of exothermic reactions are precipitation and crystallization, in which ordered solids are formed from disordered gaseous or liquid phases. In contrast, in endothermic reactions, heat is consumed from the environment. This can occur by increasing the entropy of the system, often through the formation of gaseous reaction products, which have high entropy. Since the entropy increases with temperature, many endothermic reactions preferably take place at high temperatures. On the contrary, many exothermic reactions such as crystallization occur at low temperatures. Changes in temperature can sometimes reverse the direction of a reaction, as in the Boudouard reaction:

$$\mathrm{CO_2 + C \rightleftharpoons 2\ CO}\ ; \quad \Delta H = +172.45\ \mathrm{kJ \cdot mol^{-1}}$$

This reaction between carbon dioxide and carbon to form carbon monoxide is endothermic at temperatures above approximately 800 °C and is exothermic below this temperature.

Reactions can also be characterized with the internal energy which takes into account changes in the entropy, volume and chemical potential. The latter depends, among other things, on the activities of the involved substances.

$$\mathrm{d}U = T\,dS - p\,dV + \mu\,dn$$
U: internal energy, S: entropy, p: pressure, μ: chemical potential, n: number of molecules, d: small change sign

Kinetics

The speed at which a reactions takes place is studied by reaction kinetics. The rate depends on various parameters, such as:

- Reactant concentrations, which usually make the reaction happen at a faster rate if raised through increased collisions per unit time. Some reactions, however, have rates that are *independent* of reactant concentrations. These are called zero order reactions.
- Surface area available for contact between the reactants, in particular solid ones in heterogeneous systems. Larger surface areas lead to higher reaction rates.
- Pressure – increasing the pressure decreases the volume between molecules and therefore increases the frequency of collisions between the molecules.
- Activation energy, which is defined as the amount of energy required to make the reaction start and carry on spontaneously. Higher activation energy implies that the reactants need more energy to start than a reaction with a lower activation energy.
- Temperature, which hastens reactions if raised, since higher temperature increases the energy of the molecules, creating more collisions per unit time,
- The presence or absence of a catalyst. Catalysts are substances which change the pathway (mechanism) of a reaction which in turn increases the speed of a reaction by lowering the activation energy needed for the reaction to take place. A catalyst is not destroyed or changed during a reaction, so it can be used again.

- For some reactions, the presence of electromagnetic radiation, most notably ultraviolet light, is needed to promote the breaking of bonds to start the reaction. This is particularly true for reactions involving radicals.

Several theories allow calculating the reaction rates at the molecular level. This field is referred to as reaction dynamics. The rate *v* of a first-order reaction, which could be disintegration of a substance A, is given by:

$$v = -\frac{d[\mathrm{A}]}{dt} = k \cdot [\mathrm{A}]$$

Its integration yields:

$$[\mathrm{A}](t) = [\mathrm{A}]_0 \cdot e^{-k \cdot t}$$

Here k is first-order rate constant having dimension 1/time, [A](t) is concentration at a time *t* and $[\mathrm{A}]_0$ is the initial concentration. The rate of a first-order reaction depends only on the concentration and the properties of the involved substance, and the reaction itself can be described with the characteristic half-life. More than one time constant is needed when describing reactions of higher order. The temperature dependence of the rate constant usually follows the Arrhenius equation:

$$k = k_0 e^{-E_a/k_B T}$$

where E_a is the activation energy and k_B is the Boltzmann constant. One of the simplest models of reaction rate is the collision theory. More realistic models are tailored to a specific problem and include the transition state theory, the calculation of the potential energy surface, the Marcus theory and the Rice–Ramsperger–Kassel–Marcus (RRKM) theory.

Reaction types

Oxidation and reduction

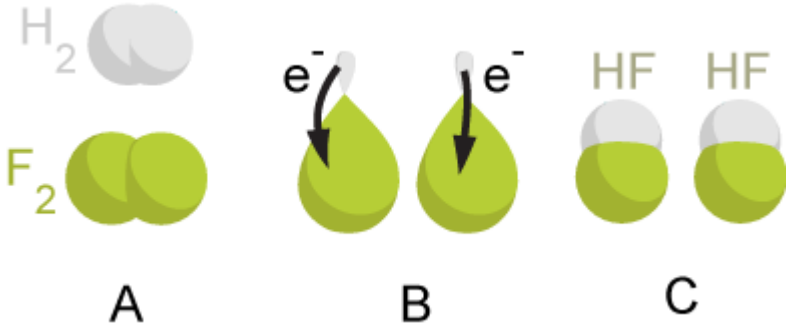
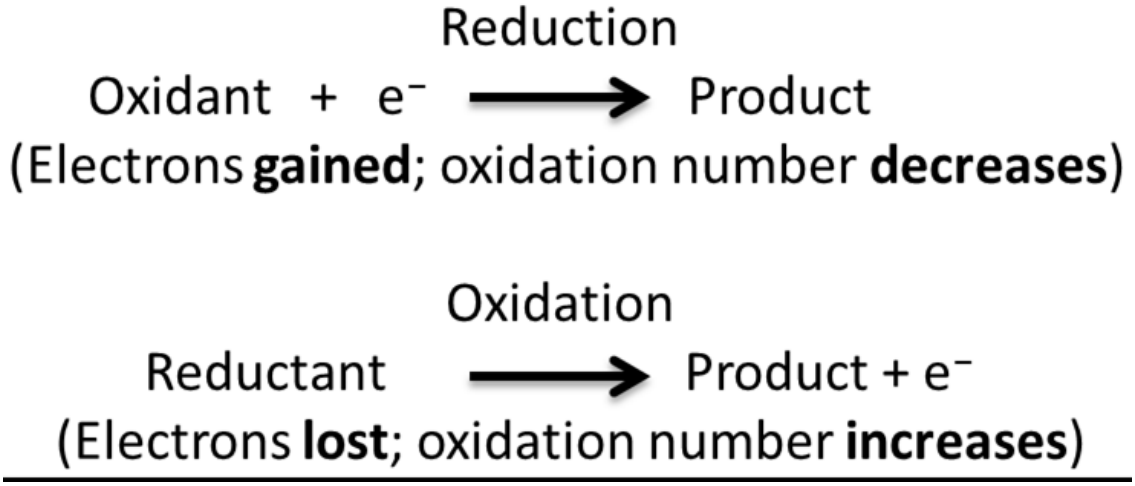


Illustration of a redox reaction



The two parts of a redox reaction

Redox reactions can be understood in terms of transfer of electrons from one involved species (reducing agent) to another (oxidizing agent). In this process, the former species is oxidized and the latter is reduced, thus the term *redox*. Though sufficient for many purposes, these descriptions are not precisely correct. Oxidation is better defined as an increase in oxidation number, and reduction as a decrease in oxidation number. In practice, the transfer of electrons will always change the oxidation number, but there are many reactions that are classed as "redox" even though no electron transfer occurs (such as those involving covalent bonds).

An example of a redox reaction is:

$$2\ S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} \rightarrow S_4O_6^{2-}{}_{(aq)} + 2\ I^-{}_{(aq)}$$

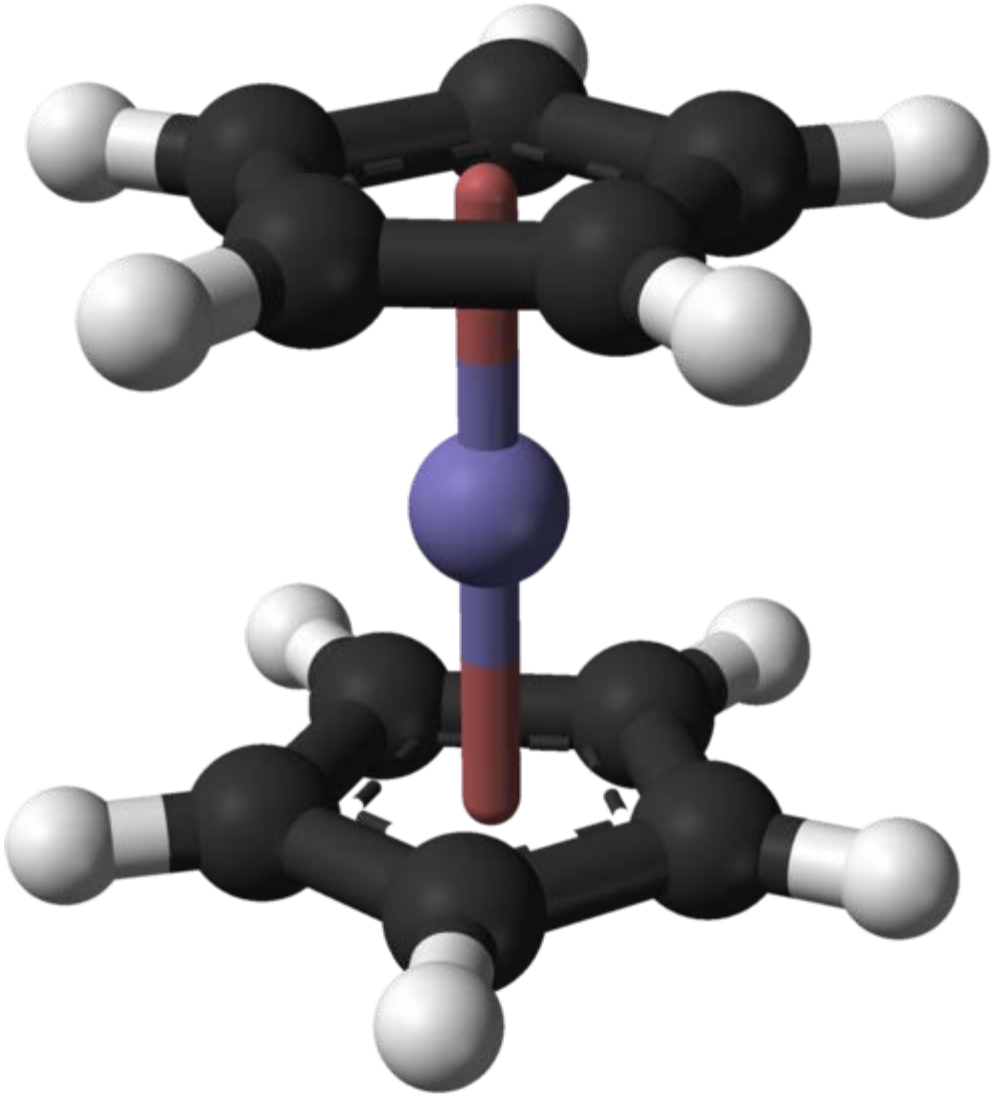
Here I_2 is reduced to I^- and $S_2O_3^{2-}$ (thiosulfate anion) is oxidized to $S_4O_6^{2-}$.

Which of the involved reactants would be reducing or oxidizing agent can be predicted from the electronegativity of their elements. Elements with low electronegativity, such as most metals, easily donate electrons and oxidize – they are reducing agents. On the contrary, many ions with high oxidation numbers, such as H_2O_2, MnO^-_4, CrO_3, $Cr_2O^{2-}_7$, OsO_4) can gain one or two extra electrons and are strong oxidizing agents.

The number of electrons donated or accepted in a redox reaction can be predicted from electron configuration of the reactant element. Elements are trying to reach the low-energy noble gas configuration, and therefore alkali metals and halogens will donate and accept one electron, respectively, and the noble gases themselves are chemically inactive.

An important class of redox reactions are the electrochemical reactions, where the electrons from the power supply are used as a reducing agent. These reactions are particularly important for the production of chemical elements, such as chlorine or aluminium. The reverse process in which electrons are released in redox reactions and can be used as electrical energy is possible and is used in the batteries.

Complexation



Ferrocene – an iron atom sandwiched between two C_5H_5 ligands

In complexation reactions, several ligands react with a metal atom to form a coordination complex. This is achieved by providing lone pairs of the ligand into empty orbitals of the metal atom and forming dipolar bonds. The ligands are Lewis bases, they can be both ions and neutral molecules, such as carbon monoxide, ammonia or water. The number of ligands that react with a central metal atom can be found using the 18-electron rule, saying that the valence shells of a transition metal will collectively accommodate 18 electrons, whereas the symmetry of the resulting complex can be predicted with the crystal field theory and ligand field theory. Complexation reactions also include ligand exchange, in which one or more ligands are replaced by another, and redox processes which change the oxidation state of the central metal atom.

Acid-base reactions

Acid-base reactions involve transfer of protons from one molecule (acid) to another (base). Here, acids act as proton donors and bases as acceptors.

$$HA + B \rightleftharpoons A^- + HB^+$$

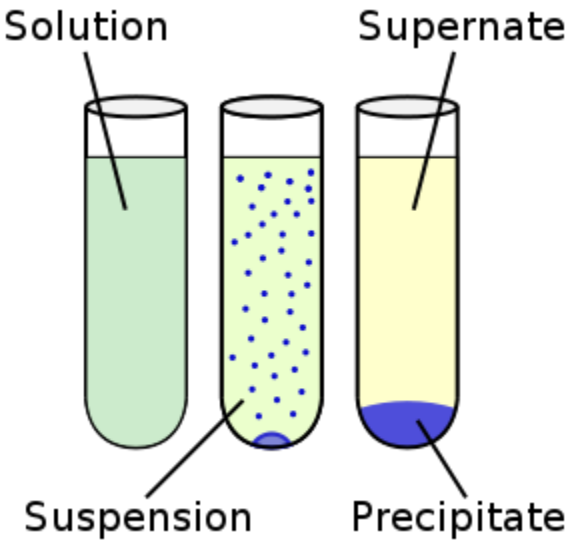
Acid-base reaction, HA: acid, B: Base, A^-: conjugated base, HB^+: conjugated acid

The associated proton transfer results in the so-called conjugate acid and conjugate base. The reverse reaction is possible, and thus the acid/base and conjugated base/acid are always in equilibrium. The equilibrium is determined by the acid and base dissociation constants (K_a and K_b) of the involved substances. A special case of the acid-base reaction is the neutralization where an acid and a base, taken at exactly same amounts, form a neutral salt.

Acid-base reactions can have different definitions depending on the acid-base concept employed. Some of the most common are:

- Arrhenius definition: Acids dissociate in water releasing H_3O^+ ions; bases dissociate in water releasing OH^- ions.
- Brønsted-Lowry definition: Acids are proton (H^+) donors, bases are proton acceptors; this includes the Arrhenius definition.
- Lewis definition: Acids are electron-pair acceptors, bases are electron-pair donors; this includes the Brønsted-Lowry definition.

Precipitation



Precipitation

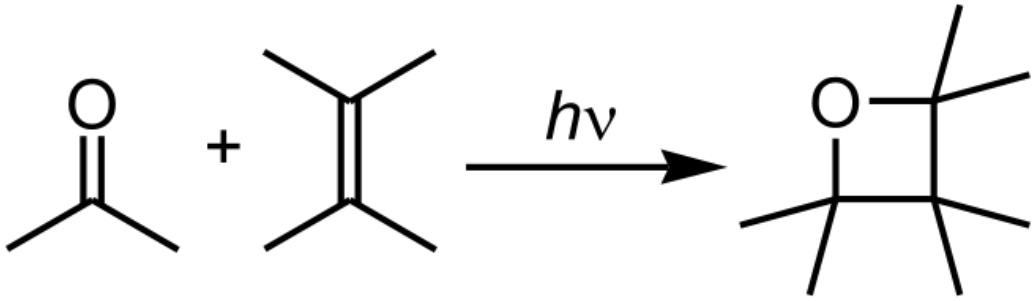
Precipitation is the formation of a solid in a solution or inside another solid during a chemical reaction. It usually takes place when the concentration of dissolved ions exceeds the solubility limit and forms an insoluble salt. This process can be assisted by adding a precipitating agent or by removal of the solvent. Rapid precipitation results in an

amorphous or microcrystalline residue and slow process can yield single crystals. The latter can also be obtained by recrystallization from microcrystalline salts.

Solid-state reactions

Reactions can take place between two solids. However, because of the relatively small diffusion rates in solids, the corresponding chemical reactions are very slow. They are accelerated by increasing the reaction temperature and finely dividing the reactant to increase the contacting surface area.

Photochemical reactions

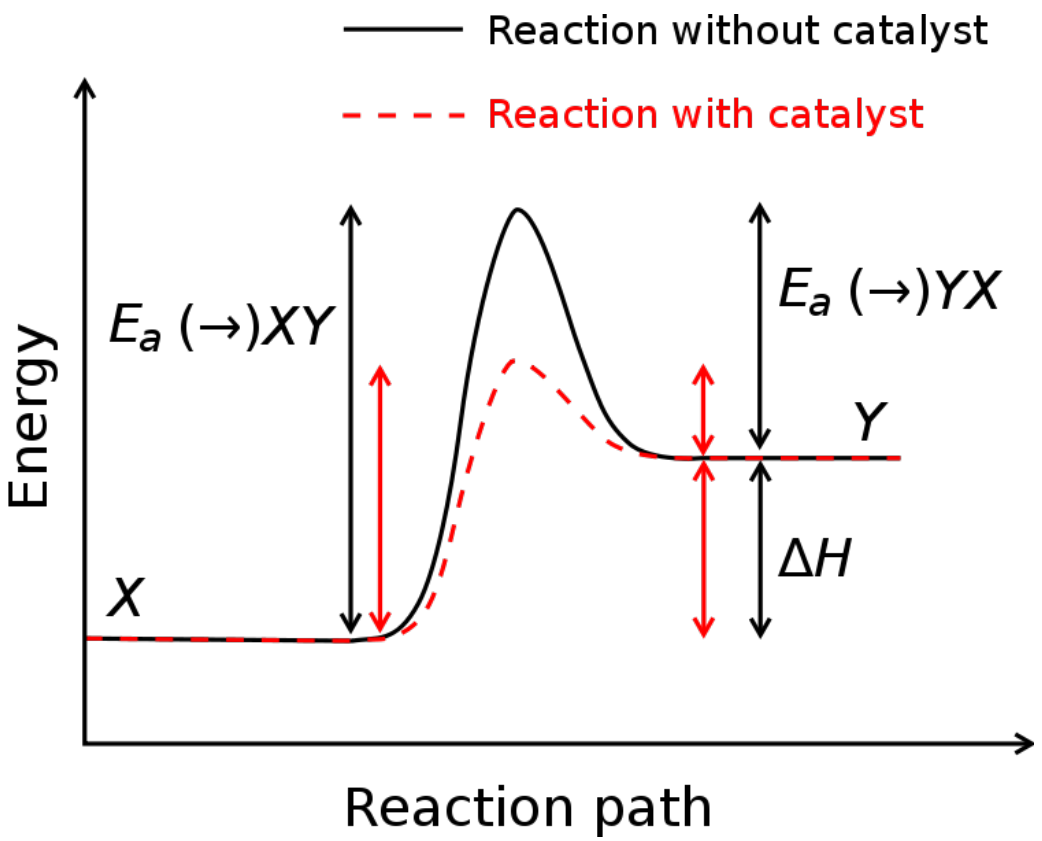


In this Paterno–Büchi reaction, a photoexcited carbonyl group is added to an unexcited olefin, yielding an oxetane.

In photochemical reactions, atoms and molecules absorb energy (photons) of the illumination light and convert into an excited state. They can then release this energy by breaking chemical bonds, thereby producing radicals. Photochemical reactions include hydrogen-oxygen reactions, radical polymerization, chain reactions and rearrangement reactions.

Many important processes involve photochemistry. The premier example is photosynthesis, in which most plants use solar energy to convert carbon dioxide and water into glucose, disposing of oxygen as a side-product. Humans rely on photochemistry for the formation of vitamin D, and vision is initiated by a photochemical reaction of rhodopsin. In fireflies, an enzyme in the abdomen catalyzes a reaction that results in bioluminescence. Many significant photochemical reactions, such as ozone formation, occur in the Earth atmosphere and constitute atmospheric chemistry.

Catalysis



Schematic potential energy diagram showing the effect of a catalyst in an endothermic chemical reaction. The presence of a catalyst opens a different reaction pathway (in red) with a lower activation energy. The final result and the overall thermodynamics are the same.

Solid heterogeneous catalysts are plated on meshes in ceramic catalytic converters in order to maximize their surface area. This exhaust converter is from a Peugeot 106 S2 1100

In catalysis, the reaction does not proceed directly, but through a third substance known as catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself; however, it can be inhibited, deactivated or destroyed by secondary processes. Catalysts can be used in a different phase (heterogeneous) or in the same phase (homogenous) as the reactants. In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid-liquid system or evaporate in a solid-gas system. Catalysts can only speed up the reaction – chemicals that slow down the reaction are called inhibitors. Substances that increase the activity of catalysts are called promoters, and substances that deactivate catalysts are called catalytic poisons. With a catalyst, a reaction which is kinetically inhibited by a high activation energy can take place in circumvention of this activation energy.

Heterogeneous catalysts are usually solids, powdered in order to maximize their surface area. Of particular importance in heterogeneous catalysis are the platinum group metals and other transition metals, which are used in hydrogenations, catalytic reforming and in the synthesis of commodity chemicals such as nitric acid and ammonia. Acids are an example of a homogeneous catalyst, they increase the nucleophilicity of carbonyls, allowing a reaction that would not otherwise proceed with electrophiles. The advantage of homogeneous catalysts is the ease of mixing them with the reactants, but they may also be difficult to separate from the products. Therefore, heterogeneous catalysts are preferred in many industrial processes.

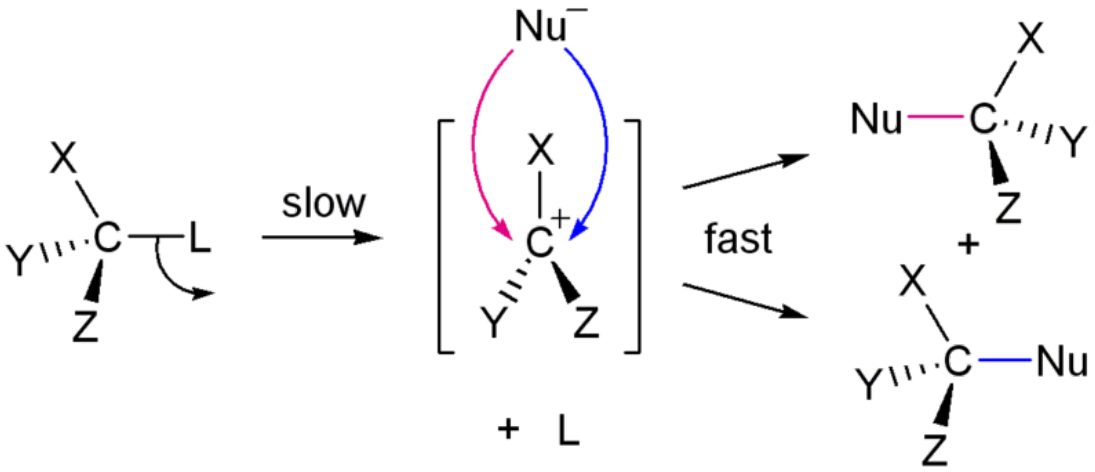
Reactions in organic chemistry

In organic chemistry, in addition to oxidation, reduction or acid-base reactions, a number of other reactions can take place which involve covalent bonds between carbon atoms or carbon and heteroatoms (such as oxygen, nitrogen, halogens, etc.). Many specific reactions in organic chemistry are name reactions designated after their discoverers.

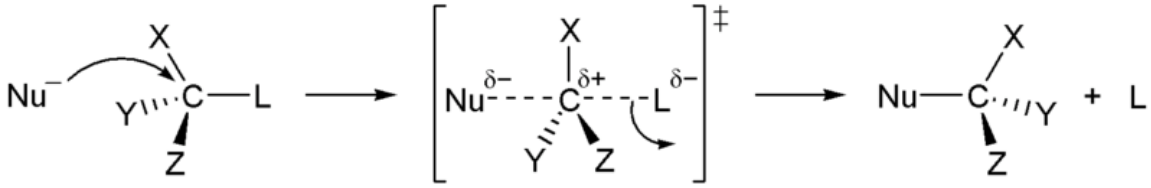
Substitution

In a substitution reaction, a functional group in a particular chemical compound is replaced by another group. These reactions can be distinguished by the type of substituting species into a nucleophilic, electrophilic or radical substitution.

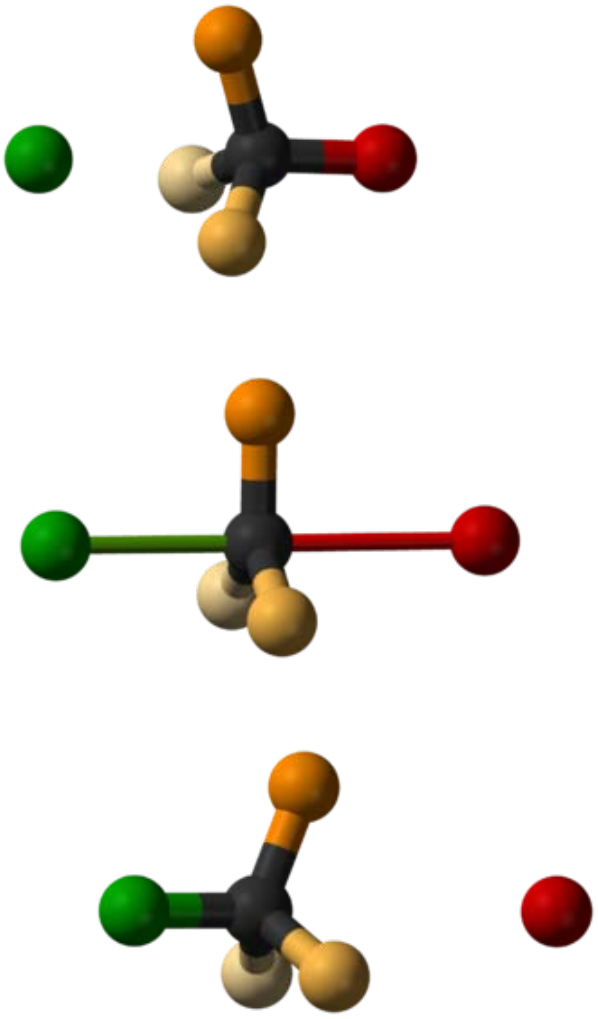
In the first type, a nucleophile, an atom or molecule with an excess of electrons and thus a negative charge or partial charge, replaces another atom or part of the "substrate" molecule. The electron pair from the nucleophile attacks the substrate forming a new bond, while the leaving group departs with an electron pair. The nucleophile may be electrically neutral or negatively charged, whereas the substrate is typically neutral or positively charged. Examples of nucleophiles are hydroxide ion, alkoxides, amines and halides. This type of reaction is found mainly in aliphatic hydrocarbons, and rarely in aromatic hydrocarbon. The latter have high electron density and enter nucleophilic aromatic substitution only with very strong electron withdrawing groups. Nucleophilic substitution can take place by two different mechanisms, S_N1 and S_N2. In their names, S stands for substitution, N for nucleophilic, and the number represents the kinetic order of the reaction, unimolecular or bimolecular.



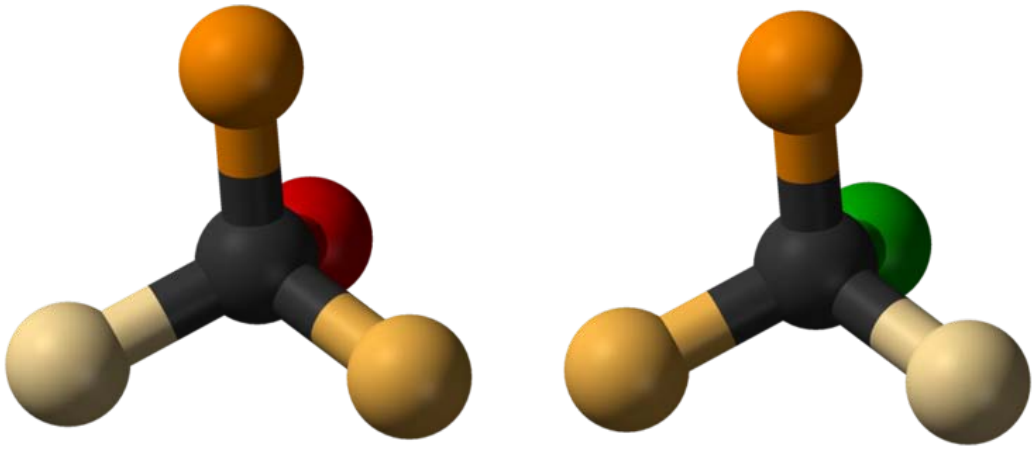
S_N1 mechanism



S_N2 mechanism



The three steps of an S_N2 reaction. The nucleophile is green and the leaving group is red

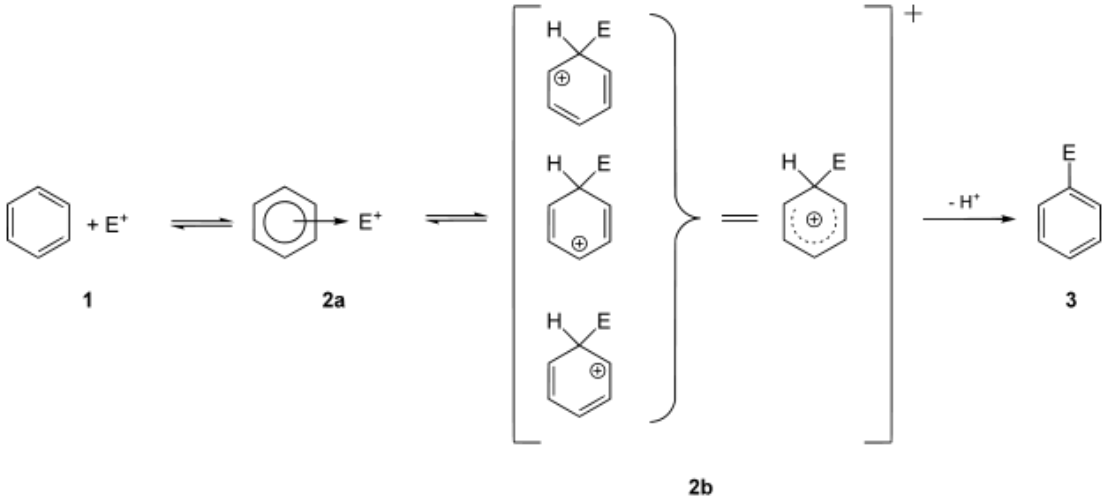


S_N2 reaction causes stereo inversion (Walden inversion)

The S_N1 reaction proceeds in two steps. First, the leaving group is eliminated creating a carbocation. This is followed by a rapid reaction with the nucleophile.

In the S_N2 mechanism, the nucleophile forms a transition state with the attacked molecule, and only then the leaving group is cleaved. These two mechanisms differ in the stereochemistry of the products. S_N1 leads to the non-stereospecific addition and does not result in a chiral center, but rather in a set of geometric isomers (*cis/trans*). In contrast, a reversal (Walden inversion) of the previously existing stereochemistry is observed in the S_N2 mechanism.

Electrophilic substitution is the counterpart of the nucleophilic substitution in that the attacking atom or molecule, an electrophile, has low electron density and thus a positive charge. Typical electrophiles are the carbon atom of carbonyl groups, carbocations or sulfur or nitronium cations. This reaction takes place almost exclusively in aromatic hydrocarbons, where it is called electrophilic aromatic substitution. The electrophile attack results in the so-called σ-complex, a transition state in which the aromatic system is abolished. Then, the leaving group, usually a proton, is split off and the aromaticity is restored. An alternative to aromatic substitution is electrophilic aliphatic substitution. It is similar to the nucleophilic aliphatic substitution and also has two major types, S_E1 and S_E2



Mechanism of electrophilic aromatic substitution

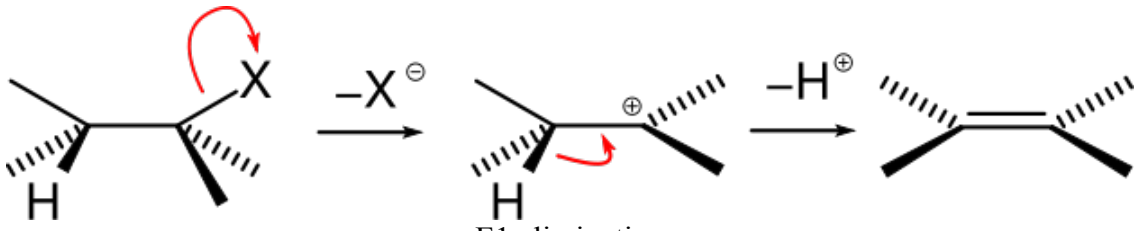
In the third type of substitution reaction, radical substitution, the attacking particle is a radical. This process usually takes the form of a chain reaction, for example in the reaction of alkanes with halogens. In the first step, light or heat disintegrates the halogen-containing molecules producing the radicals. Then the reaction proceeds as an avalanche until two radicals meet and recombine.

$$\mathrm{X}\cdot + \mathrm{R{-}H} \longrightarrow \mathrm{X{-}H} + \mathrm{R}\cdot$$
$$\mathrm{R}\cdot + \mathrm{X_2} \longrightarrow \mathrm{R{-}X} + \mathrm{X}\cdot$$

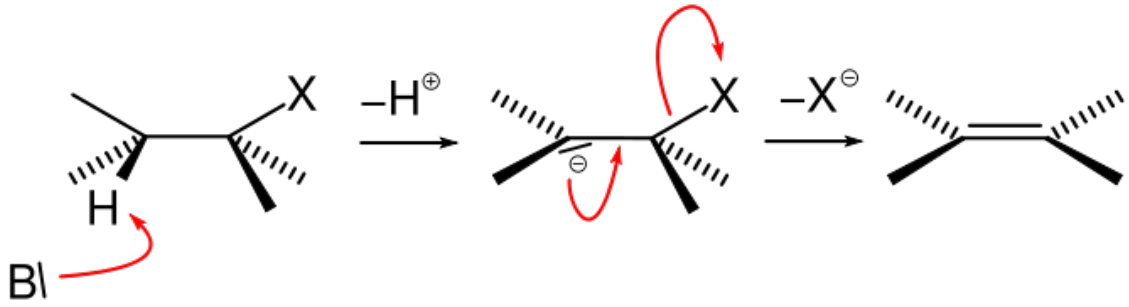
Reactions during the chain reaction of radical substitution

Addition and elimination

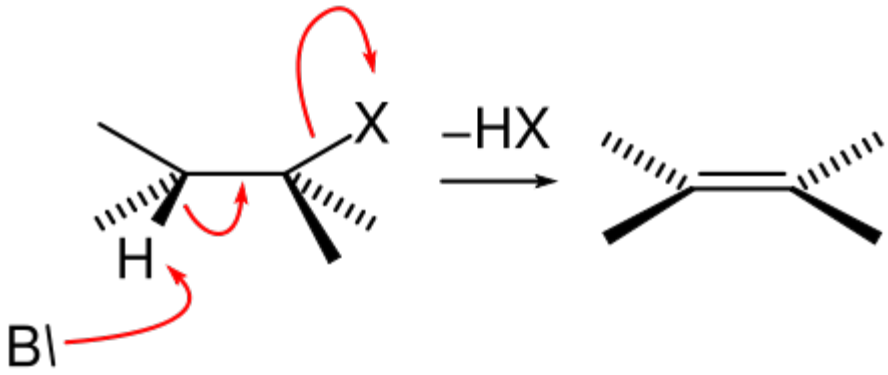
The addition and its counterpart, the elimination, are reactions which change the number of substituents on the carbon atom, and form or cleave multiple bonds. Double and triple bonds can be produced by eliminating a suitable leaving group. Similar to the nucleophilic substitution, there are several possible reaction mechanisms which are named after the respective reaction order. In the E1 mechanism, the leaving group is ejected first, forming a carbocation. The next step, formation of the double bond, takes place with elimination of a proton (deprotonation). The leaving order is reversed in the E1cb mechanism, that is the proton is split off first. This mechanism requires participation of a base. Because of the similar conditions, both reactions in the E1 or E1cb elimination always compete with the S_N1 substitution.



E1 elimination



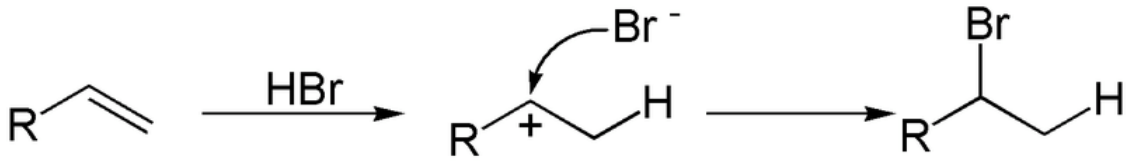
E1cb elimination



E2 elimination

The E2 mechanism also requires a base, but there the attack of the base and the elimination of the leaving group proceed simultaneously and produce no ionic

intermediate. In contrast to the E1 eliminations, different stereochemical configurations are possible for the reaction product in the E2 mechanism, because the attack of the base preferentially occurs in the anti-position with respect to the leaving group. Because of the similar conditions and reagents, the E2 elimination is always in competition with the S_N2-substitution.

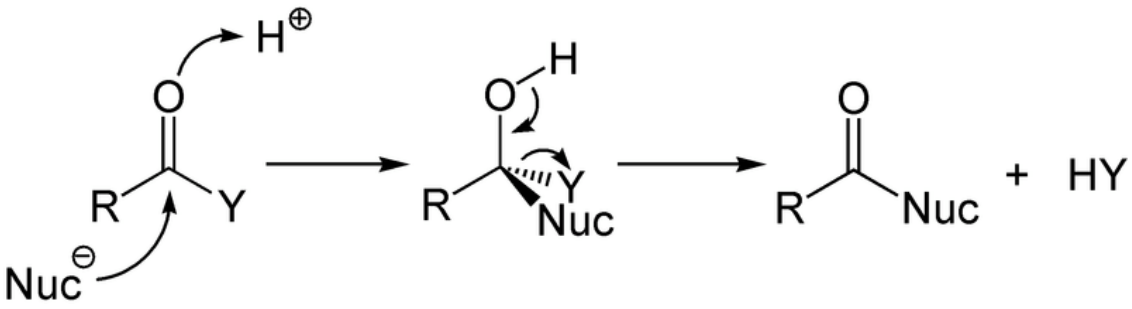


Electrophilic addition of hydrogen bromide

The counterpart of elimination is the addition where double or triple bonds are converted into single bonds. Similar to the substitution reactions, there are several types of additions distinguished by the type of the attacking particle. For example, in the electrophilic addition of hydrogen bromide, an electrophile (proton) attacks the double bond forming a carbocation, which then reacts with the nucleophile (bromine). The carbocation can be formed on either side of the double bond depending on the groups attached to its ends, and the preferred configuration can be predicted with the Markovnikov's rule. This rule states that "In the heterolytic addition of a polar molecule to an alkene or alkyne, the more electronegative (nucleophilic) atom (or part) of the polar molecule becomes attached to the carbon atom bearing the smaller number of hydrogen atoms."

If the addition of a functional group takes place at the less substituted carbon atom of the double bond, then the electrophilic substitution with acids is not possible. In this case, one has to use the hydroboration–oxidation reaction, where in the first step, the boron atom acts as electrophile and adds to the less substituted carbon atom. At the second step, the nucleophilic hydroperoxide or halogen anion attacks the boron atom.

While the addition to the electron-rich alkenes and alkynes is mainly electrophilic, the nucleophilic addition plays an important role for the carbon-heteroatom multiple bonds, and especially its most important representative, the carbonyl group. This process is often associated with an elimination, so that after the reaction the carbonyl group is present again. It is therefore called addition-elimination reaction and may occur in carboxylic acid derivatives such as chlorides, esters or anhydrides. This reaction is often catalyzed by acids or bases, where the acids increase by the electrophilicity of the carbonyl group by binding to the oxygen atom, whereas the bases enhance the nucleophilicity of the attacking nucleophile.

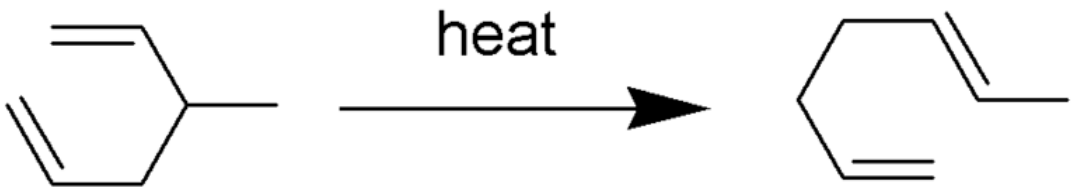


Acid-catalyzed addition-elimination mechanism

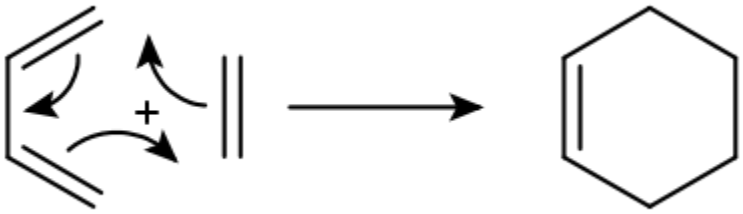
Nucleophilic addition of a carbanion or another nucleophile to the double bond of an alpha, beta unsaturated carbonyl compound can proceed via the Michael reaction, which belongs to the larger class of conjugate additions. This is one of the most useful methods for the mild formation of C-C bonds.

Some additions which can not be executed with nucleophiles and electrophiles, can be succeeded with free radicals. As with the free-radical substitution, the radical addition proceeds as a chain reaction, and such reactions are the basis of the free-radical polymerization.

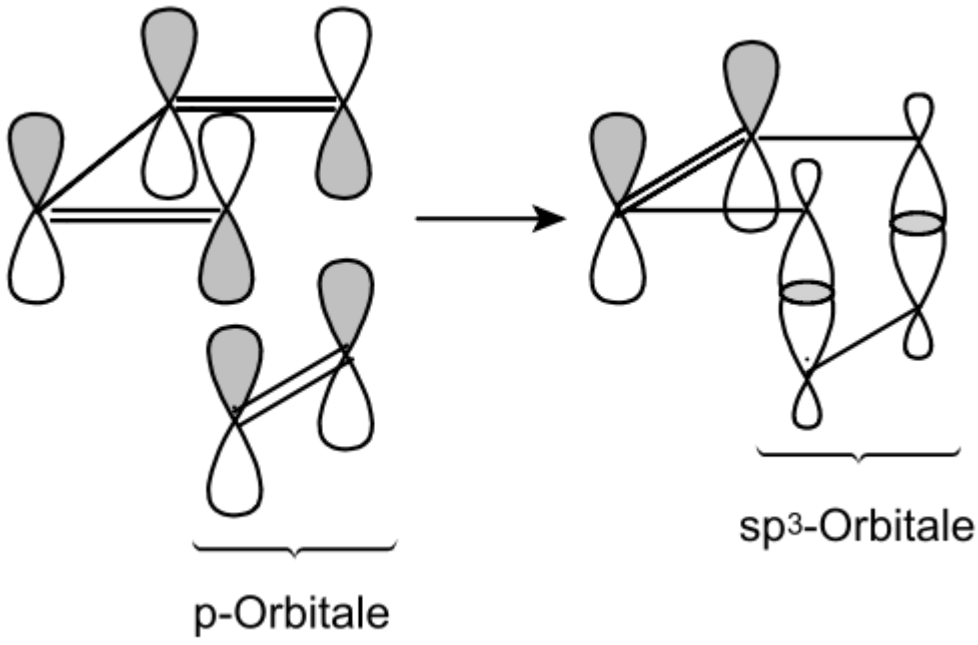
Other organic reaction mechanisms



The Cope rearrangement of 3-methyl-1,5-hexadiene



Mechanism of a Diels-Alder reaction



Orbital overlap in a Diels-Alder reaction

In a rearrangement reaction, the carbon skeleton of a molecule is rearranged to give a structural isomer of the original molecule. These include hydride shift reactions such as the Wagner-Meerwein rearrangement, where a hydrogen, alkyl or aryl group migrates from one carbon to a neighboring carbon. Most rearrangements are associated with the breaking and formation of new carbon-carbon bonds. Other examples are sigmatropic reaction such as the Cope rearrangement.

Cyclic rearrangements include cycloadditions and, more generally, pericyclic reactions, wherein two or more double bond-containing molecules form a cyclic molecule. An important example of cycloaddition reaction is the Diels–Alder reaction (the so-called [4+2] cycloaddition) between a conjugated diene and a substituted alkene to form a substituted cyclohexene system.

Whether or not a certain cycloaddition would proceed depends on the electronic orbitals of the participating species, as only orbitals with the same sign of wave function will overlap and interact constructively to form new bonds. Cycloaddition is usually assisted by light or heat. These perturbations result in different arrangement of electrons in the excited state of the involved molecules and therefore in different effects. For example, the [4+2] Diels-Alder reactions can be assisted by heat whereas the [2+2] cycloaddition is selectively induced by light. Because of the orbital character, the potential for developing stereoisomeric products upon cycloaddition is limited, as described by the Woodward-Hoffmann rules.

Biochemical reactions

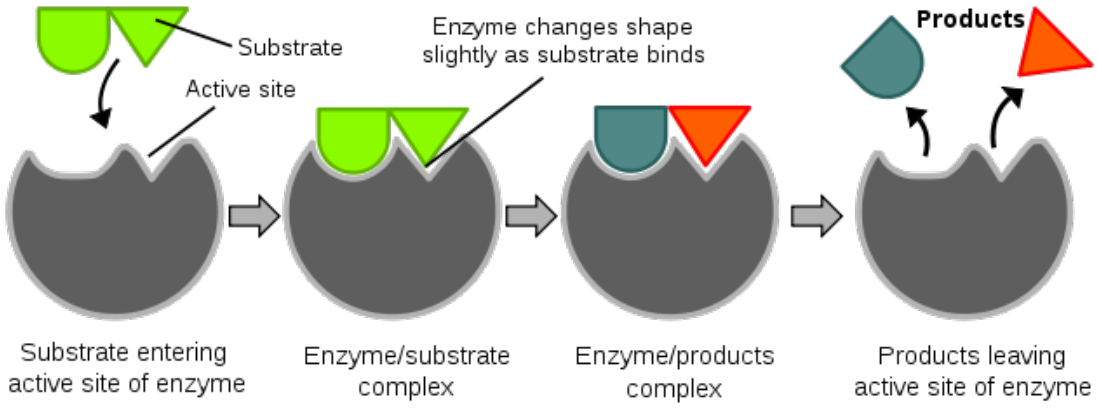


Illustration of the induced fit model of enzyme activity

Biochemical reactions are mainly controlled by enzymes. These proteins can specifically catalyze a single reaction, so that reactions can be controlled very precisely. The reaction takes place in the active site, a small part of the enzyme which is usually found in a cleft or pocket lined by amino acid residues, and the rest of the enzyme is used mainly for stabilization. The catalytic action of enzymes relies on several mechanisms including the molecular shape ("induced fit"), bond strain, proximity and orientation of molecules relatively to the enzyme, proton donation or withdrawal (acid/base catalysis), electrostatic interactions and many others.

The biochemical reactions that occur in living organisms are collectively known as metabolism. Among the most important its mechanisms is the anabolism, in which different DNA and enzyme-controlled processes result in the production of large molecules such as proteins and carbohydrates from smaller units. Bioenergetics studies the sources of energy for such reactions. An important energy sources is glucose, which can be produced by plants via photosynthesis or assimilated from food. All organisms use this energy to produce adenosine triphosphate (ATP), which can then be used to energise other reactions.

Applications

Thermite reaction proceeding in railway welding. Shortly after this, the liquid iron flows into the mould around the rail gap

Chemical reactions are central to chemical engineering where they are used for the synthesis of new compounds from natural raw materials such as petroleum and mineral ores. It is essential to make the reaction as efficient as possible, maximizing the yield and minimizing the amount of reagents, energy inputs and waste. Catalysts are especially helpful for reducing the energy required for the reaction and increasing its reaction rate.

Some specific reactions have their niche applications. For example, the thermite reaction is used to generate light and heat in pyrotechnics and welding. Although it is less controllable than the more conventional oxy-fuel welding, arc welding and flash welding, it requires much less equipment and is still used to mend rails, especially in remote areas.

Monitoring

Mechanisms of monitoring chemical reactions depend strongly on the reaction rate. Relatively slow processes can be analyzed in situ for the concentrations and identities of the individual ingredients. Important tools of real time analysis are the measurement of pH and analysis of optical absorption (color) and emission spectra. A less accessible but rather efficient method is introduction of a radioactive isotope into the reaction and monitoring how it changes over time and where it moves to; this method is often used to analyze redistribution of substances in the human body. Faster reactions are usually studied with ultrafast laser spectroscopy where utilization of femtosecond lasers allows short-lived transition states to be monitored at time scaled down to a few femtoseconds.