Essence, Principles and Basics of
Chemical Engineering

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Chapter 1

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

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

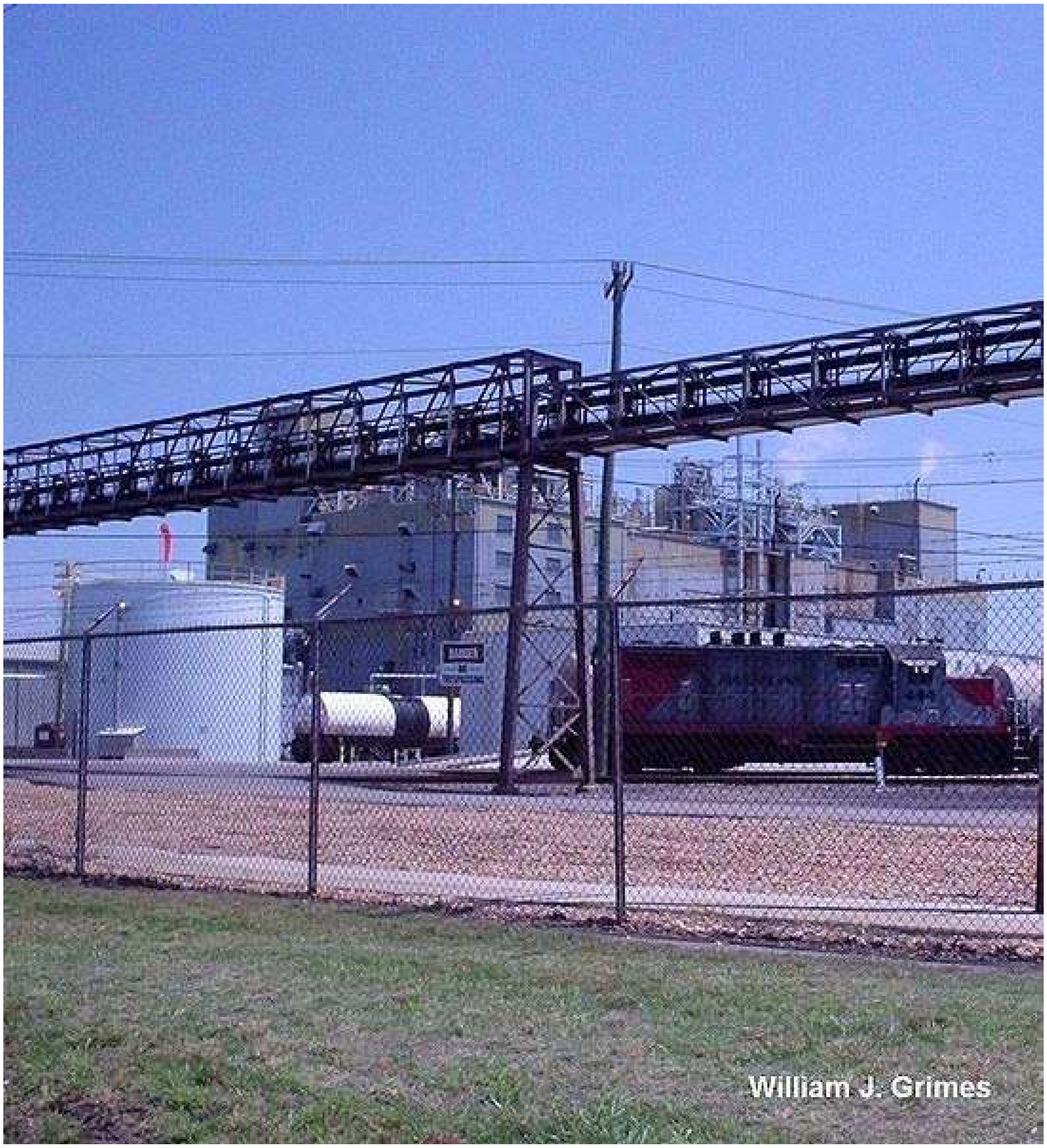
Common name	**Systematic name**	**Chemical formula**	**Chemical structure**	**CAS registry number**	**InChI**
alcohol, or ethyl alcohol	ethanol	C_2H_5OH		[64-17-5]	1/C2H6O/c1-2-3/h3H,2H2,1H3

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

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.

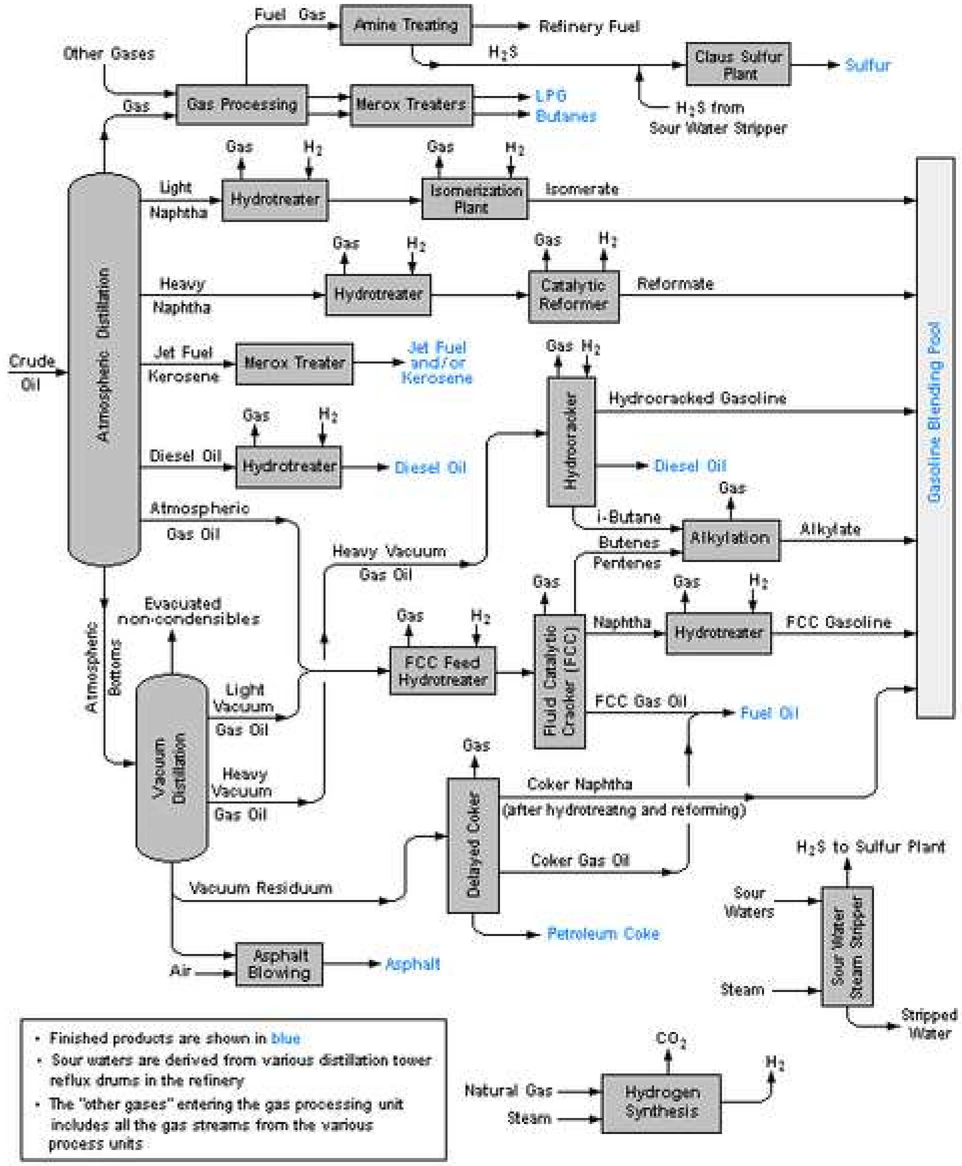
Distillation plant in Italy

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.

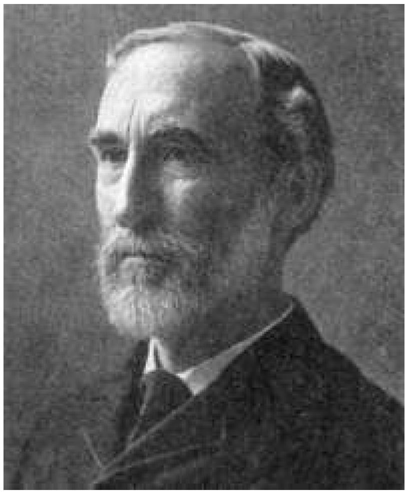
Chapter 3

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 "ΔG", 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 { ξ_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* $d\xi_j/dt$. For each and every *physically independent process* (Prigogine & Defay, p. 38; Prigogine, p. 24)

$$\mathbb{A}\ \dot{\xi} \le 0\ .$$

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 4

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.

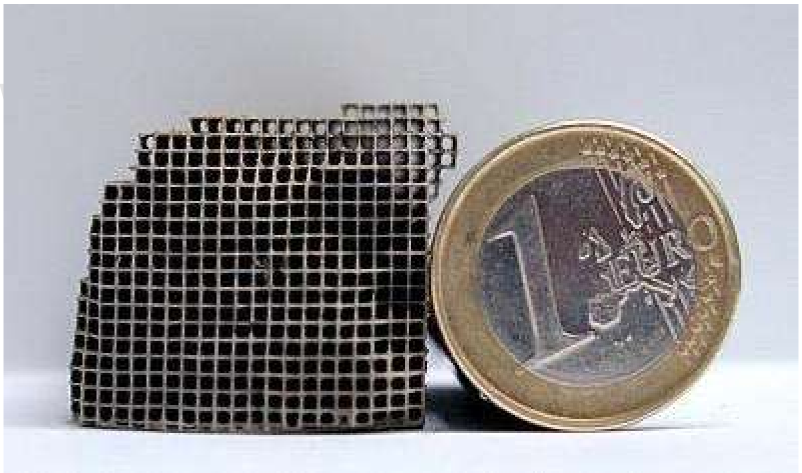
The conservation of both relativistic and invariant mass applies even to systems of particles created by pair production, where energy for new particles may come from kinetic energy of other particles, or from a photon as part of a system. Again, neither the relativistic nor the invariant mass of closed 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.

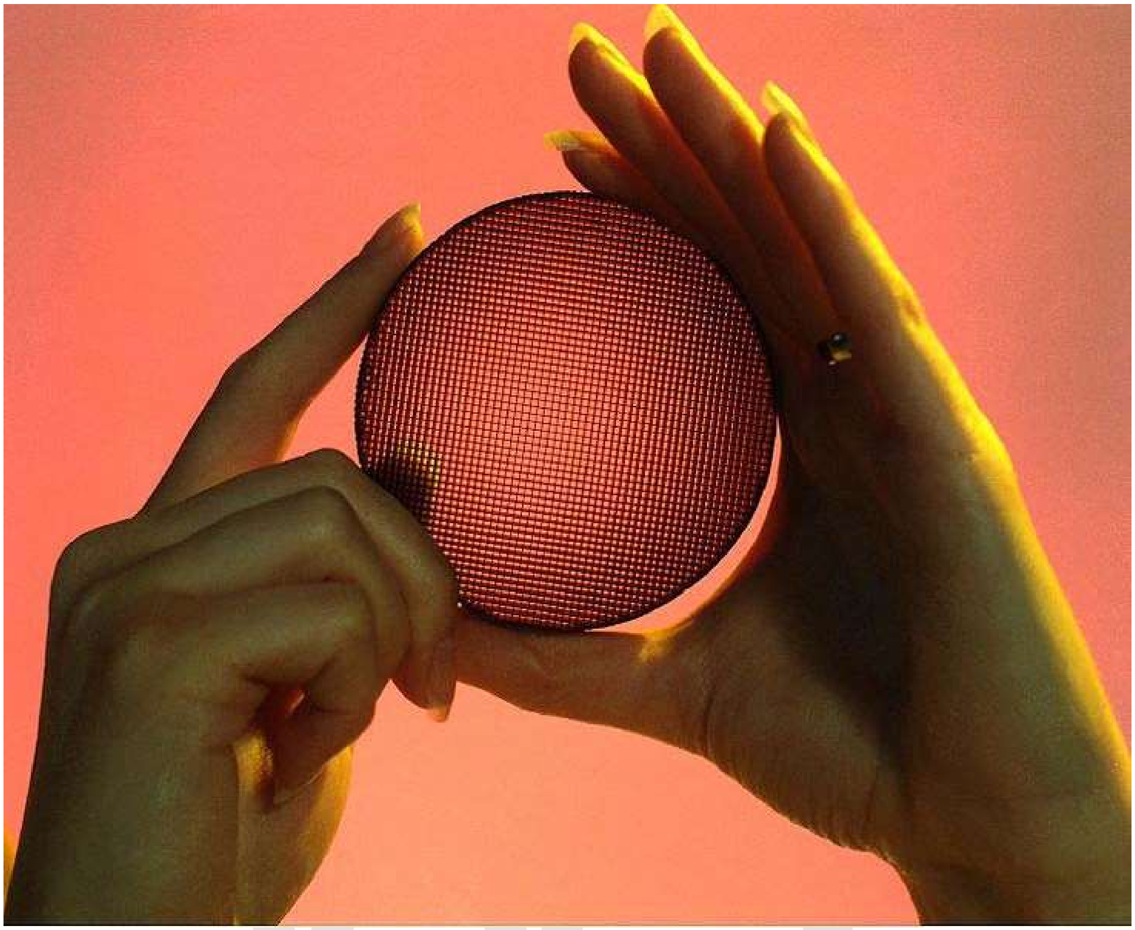
The formula implies that bound systems have an invariant mass (rest mass for the system) less than the sum of their parts, if the binding energy has been allowed to escape the system after the system has been bound. This may happen by converting system potential energy into some other kind of active 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 5

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:

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

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

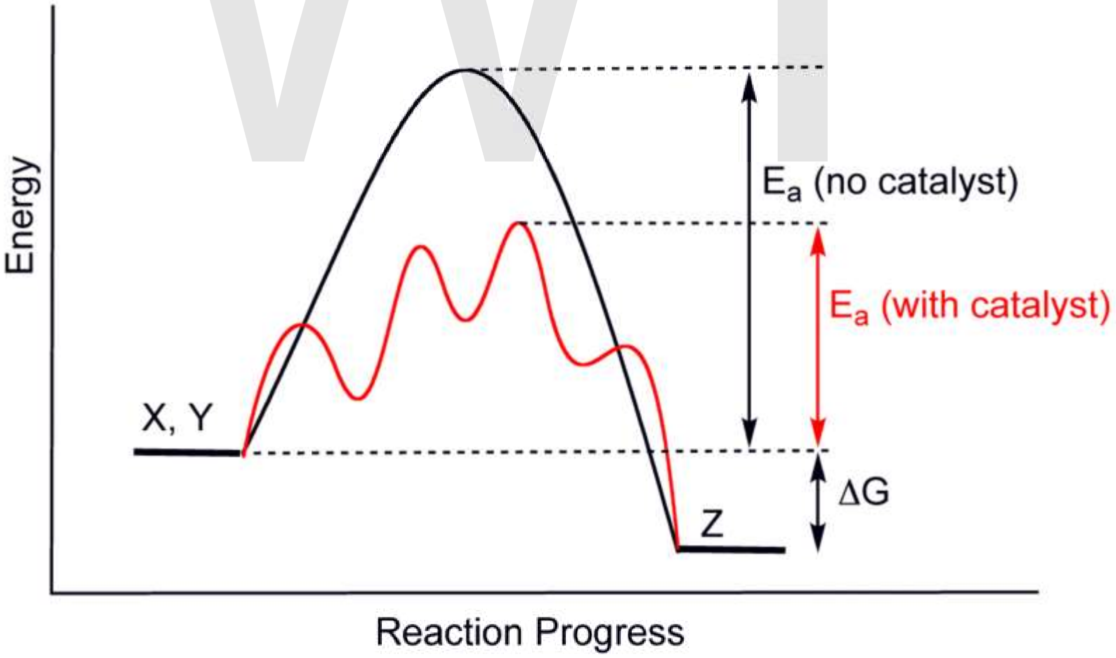
Although the catalyst is consumed by reaction 1, it is subsequently produced by reaction 4, so for the overall reaction:

$X + Y \rightarrow Z$

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 6

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.

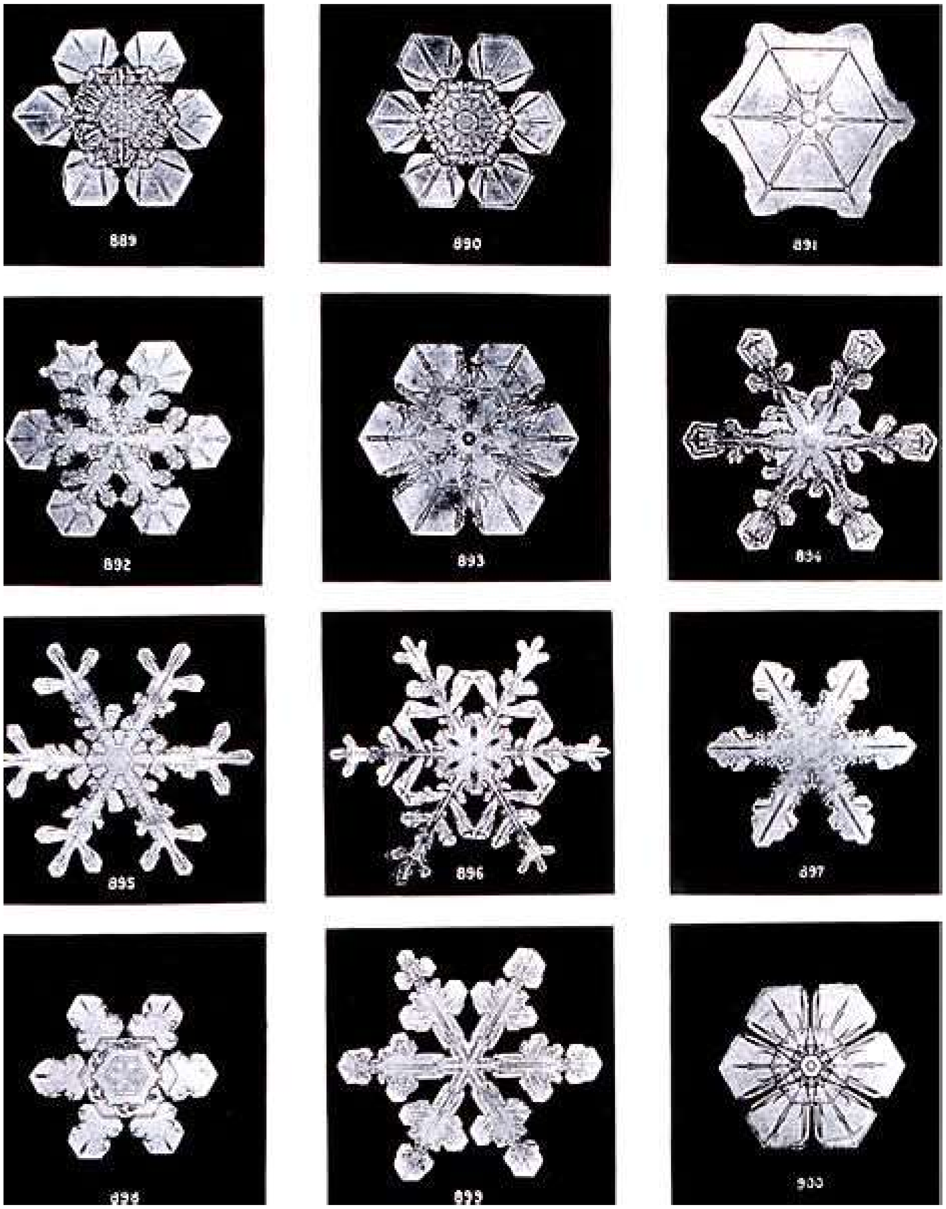
Process

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.

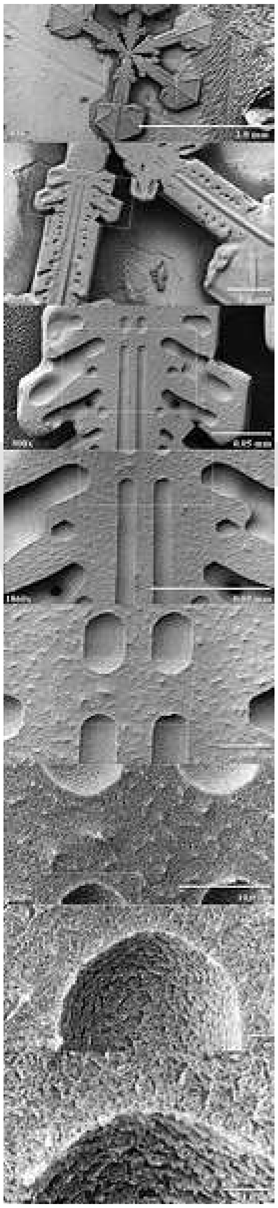
Purification

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

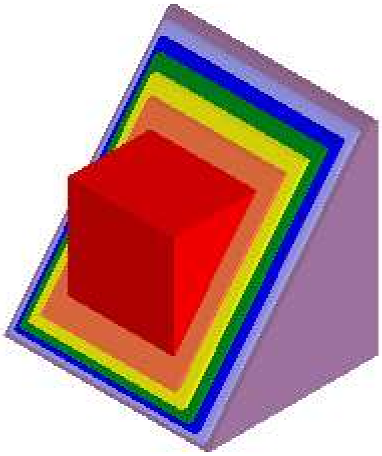
Secondary nucleation is the formation of nuclei attributable to the influence of the existing microscopic crystals in the magma. The first type of known secondary crystallization is attributable to fluid shear, the other due to collisions between already existing crystals with either a solid surface 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

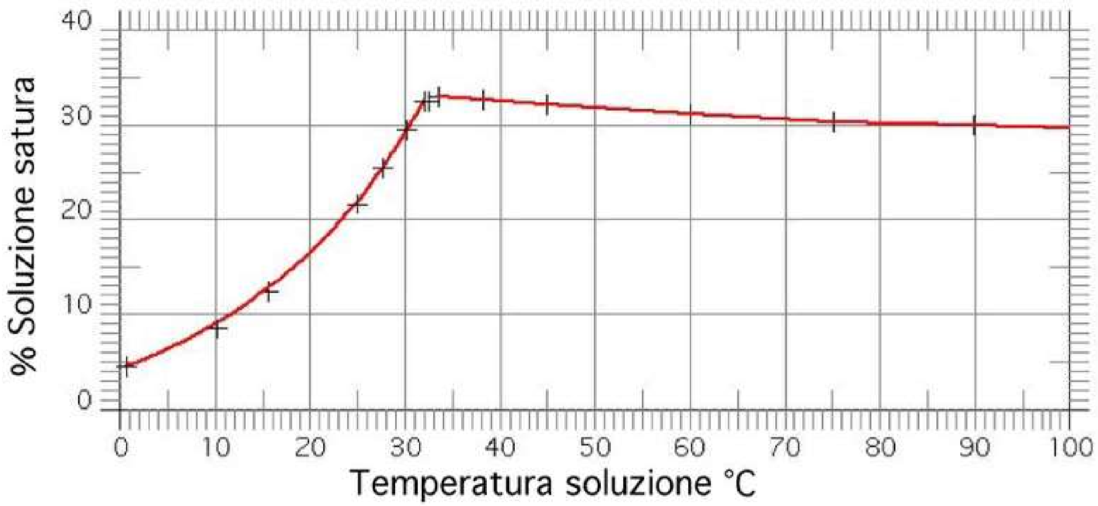
This division is not really clear-cut, since hybrid systems exist, where cooling is performed through evaporation, thus obtaining at the same time a concentration of the solution.

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).

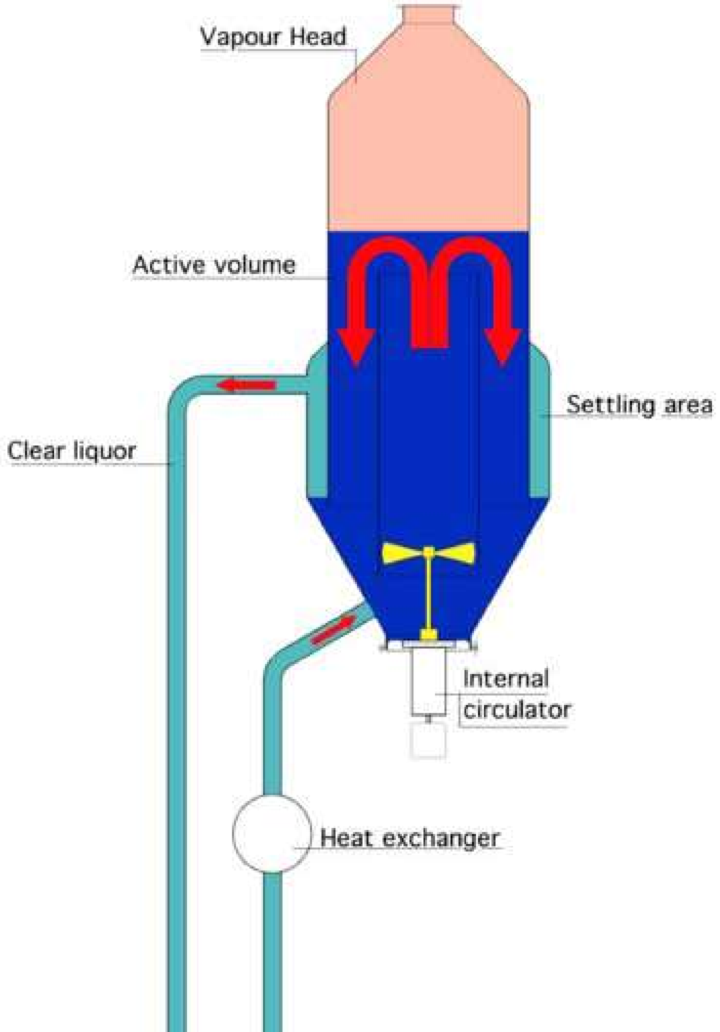
All considerations on control of crystallization parameters are the same as for the cooling models.

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

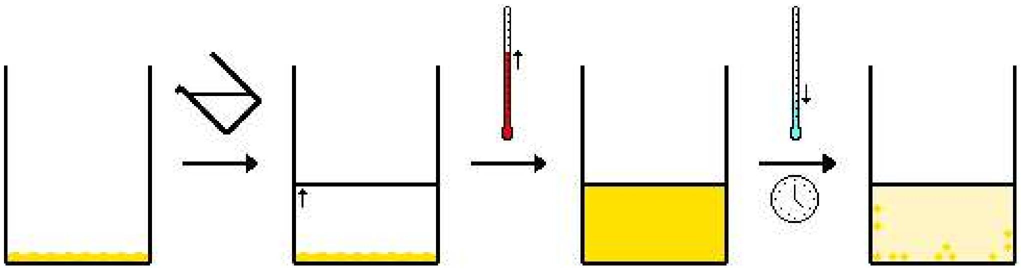
DTB Crystallizer



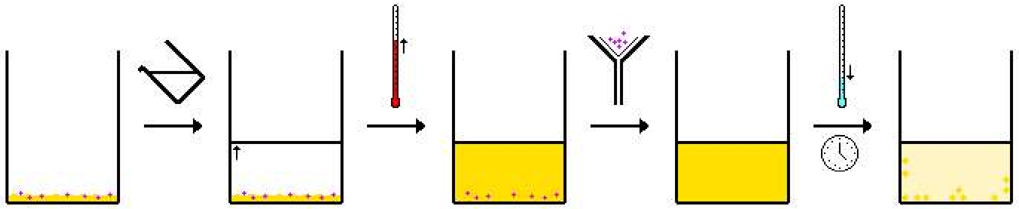
Schematic of DTB

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.

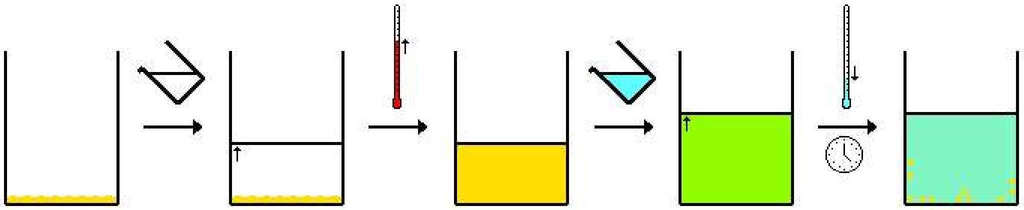
Solvent recrystallisation



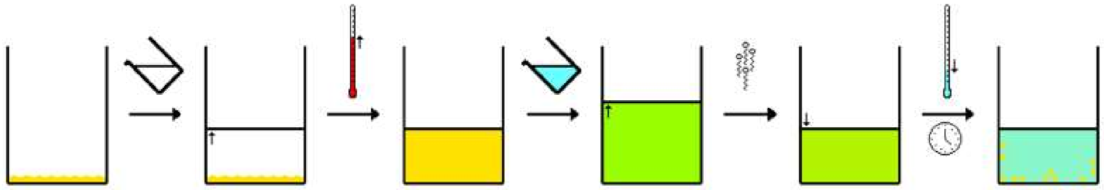
The process



Hot-filtration, 1 solvent

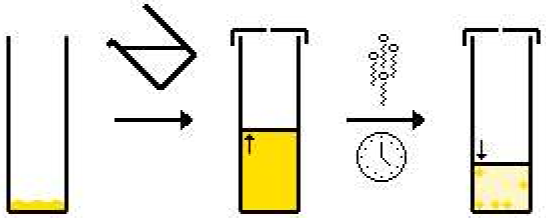


2 solvent

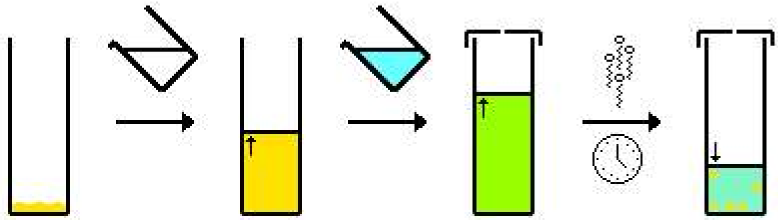


2 solvent, with evaporation

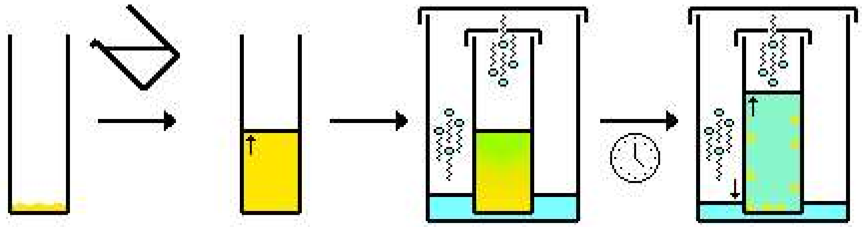
X-ray crystals



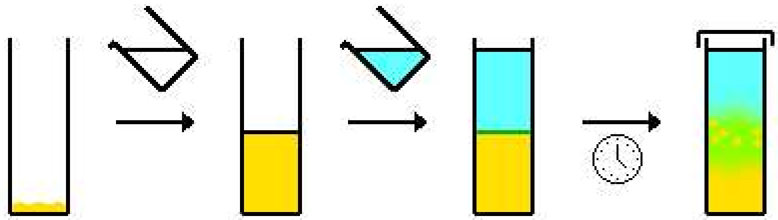
slow evaporation 1 solvent



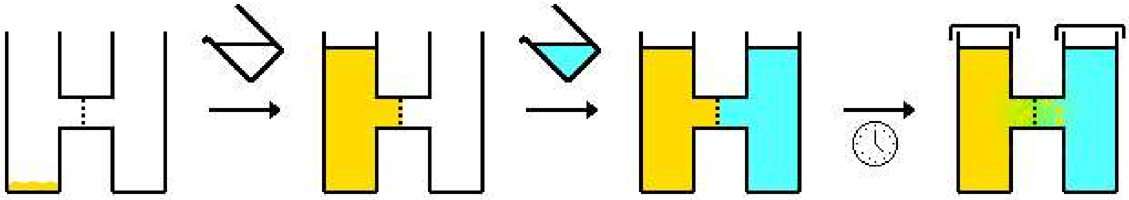
slow evaporation 2 solvent



slow gas diffusion 2 solvent



slow liquid diffusion



slow liquid diffusion - H Tube

Chapter 7

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.

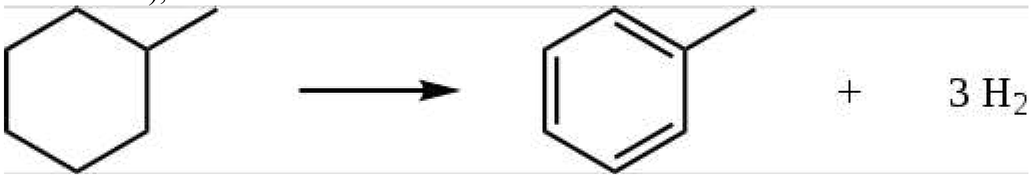
The reaction chemistry

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.

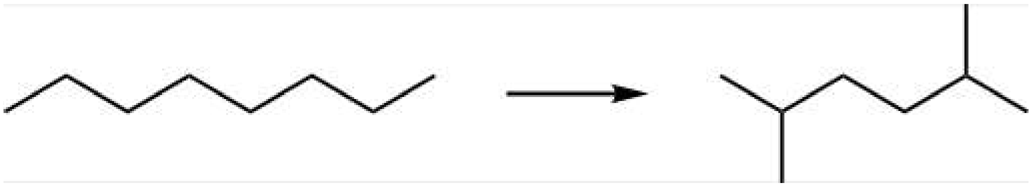
The commonly used catalytic reforming catalysts contain noble metals such as platinum and/or rhenium, which are very susceptible to poisoning by sulfur and nitrogen compounds. Therefore, the naphtha feedstock to a catalytic reformer is always pre-processed in a hydrodesulfurization unit which removes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

The four major catalytic reforming reactions are:

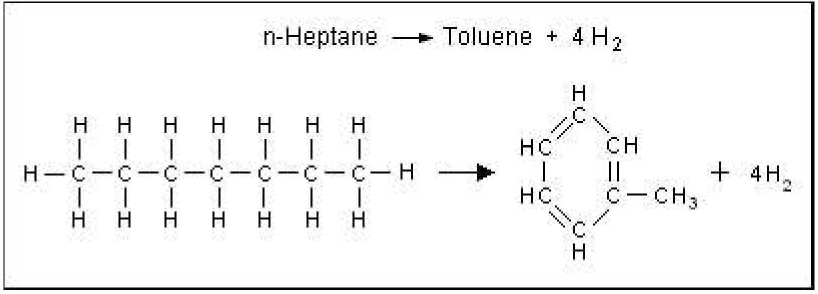
1: The dehydrogenation of naphthenes to convert them into aromatics as exemplified in the conversion methylcyclohexane (a naphthene) to toluene (an aromatic), as shown below:



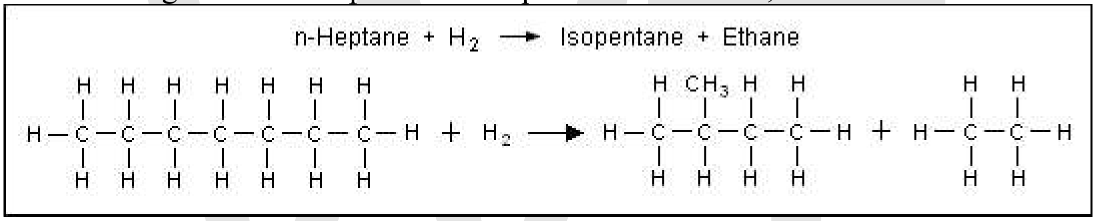
2: The isomerization of normal paraffins to isoparaffins as exemplified in the conversion of normal octane to 2,5-Dimethylhexane (an isoparaffin), as shown below:



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

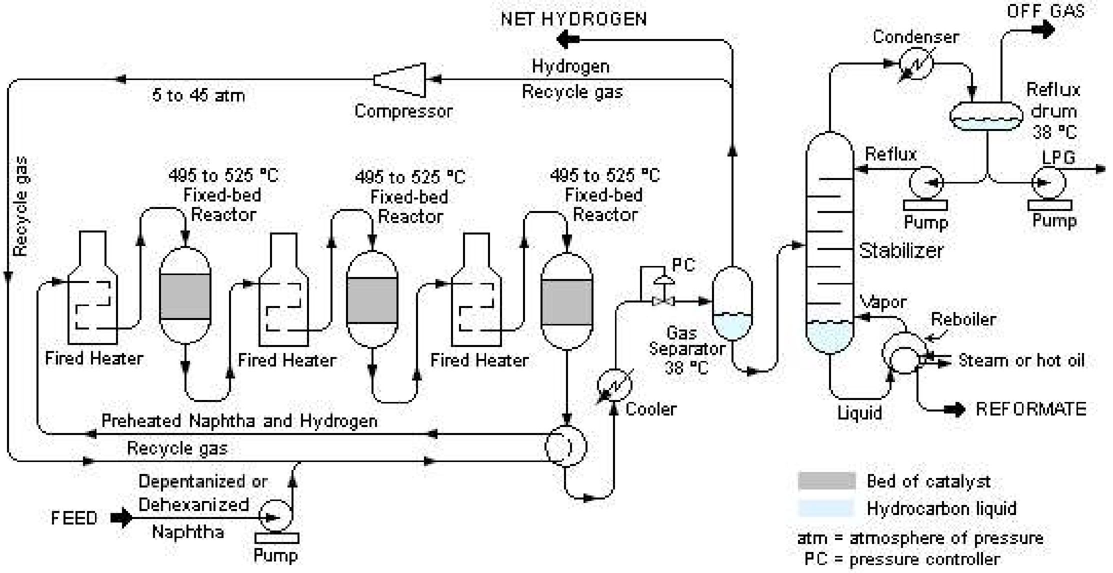
The most commonly used type of catalytic reforming unit has three reactors, each with a fixed bed of catalyst, and all of the catalyst is regenerated *in situ* during routine catalyst regeneration shutdowns which occur approximately once each 6 to 24 months. Such a unit is referred to as a semi-regenerative 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 8

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.

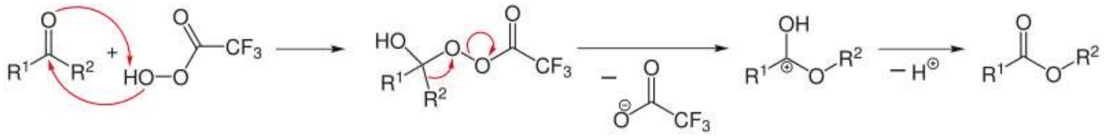
Regarding the organic chemistry, it was long believed that compounds obtained from living organisms were too complex to be obtained synthetically. According to the concept of vitalism, organic matter was endowed with a "vital force" and distinguished from inorganic materials. This separation was ended 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 ($\rightleftharpoons$) 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.

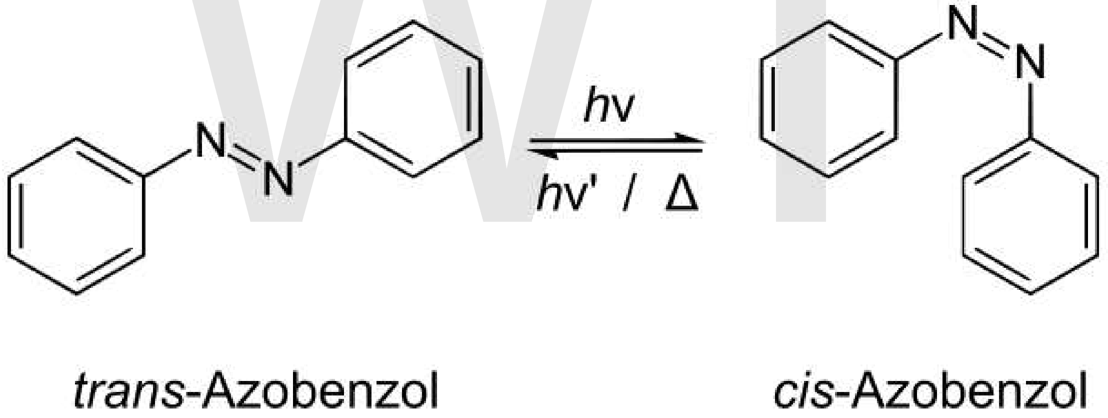


An example of organic reaction: oxidation of ketones to esters with peroxycarboxylic acid

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

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

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:

$$\Delta \mathrm{G} = \Delta \mathrm{H} - \mathrm{T} \cdot \Delta \mathrm{S}$$

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:

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

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

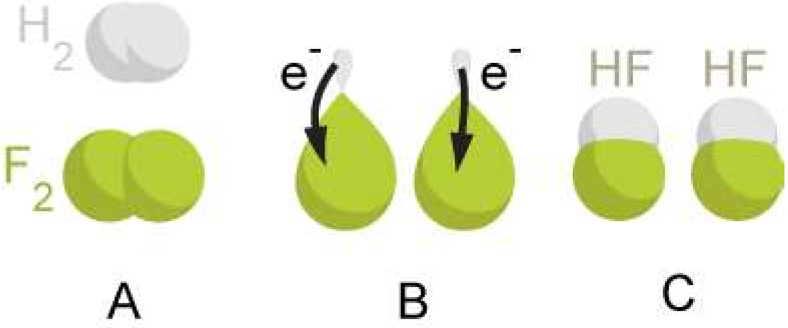
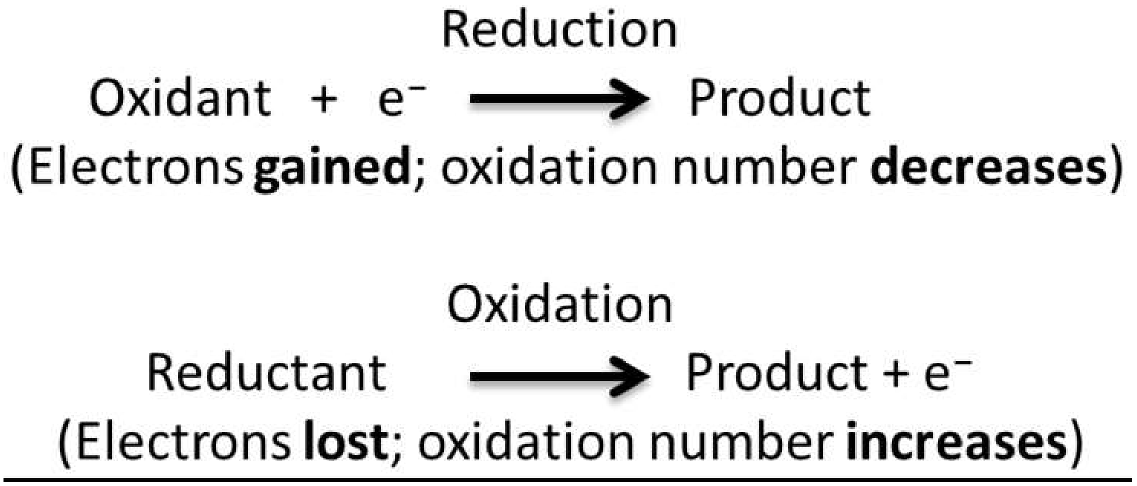


Illustration of a redox reaction



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:

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

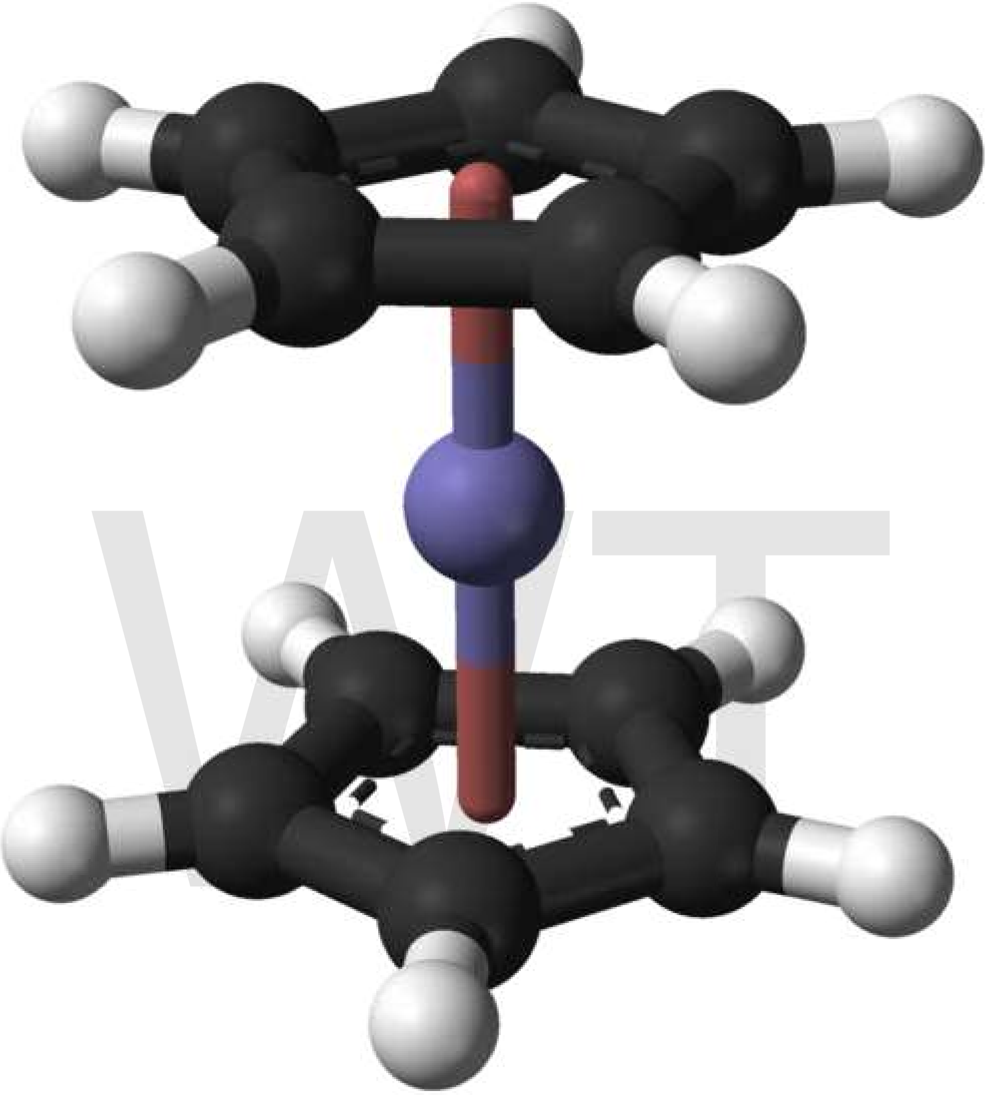
Here I_2 is reduced to I^- and $S_2O_3{}^{2-}$ (thiosulfate anion) is oxidized to $S_4O_6{}^{2-}$.

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_2O2–7, 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.

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

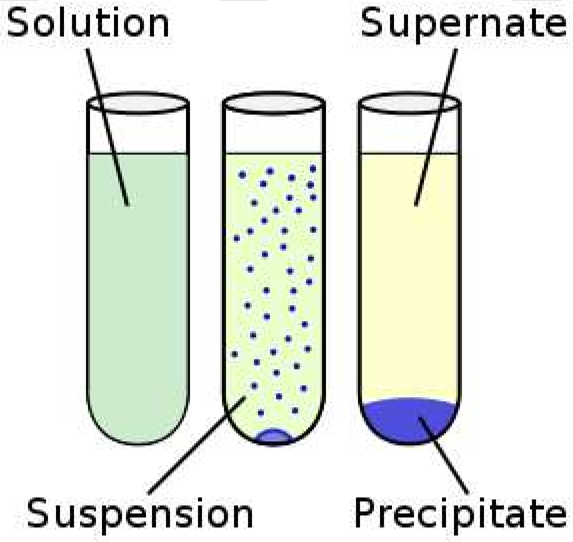
Acid-base reaction, HA: acid, B: Base, A^-: conjugated base, HB^+: conjugated acid

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



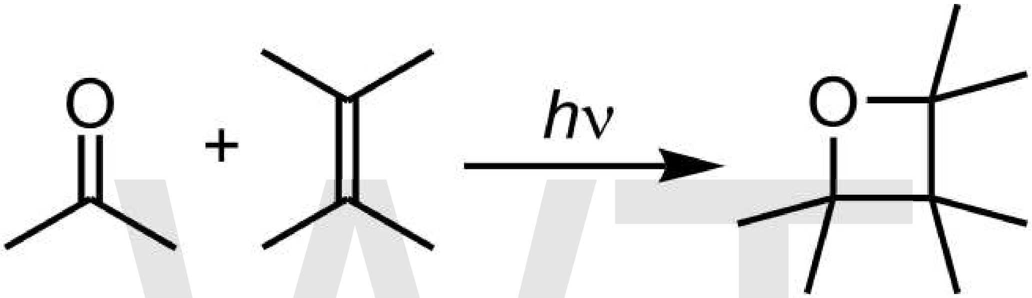
Precipitation

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

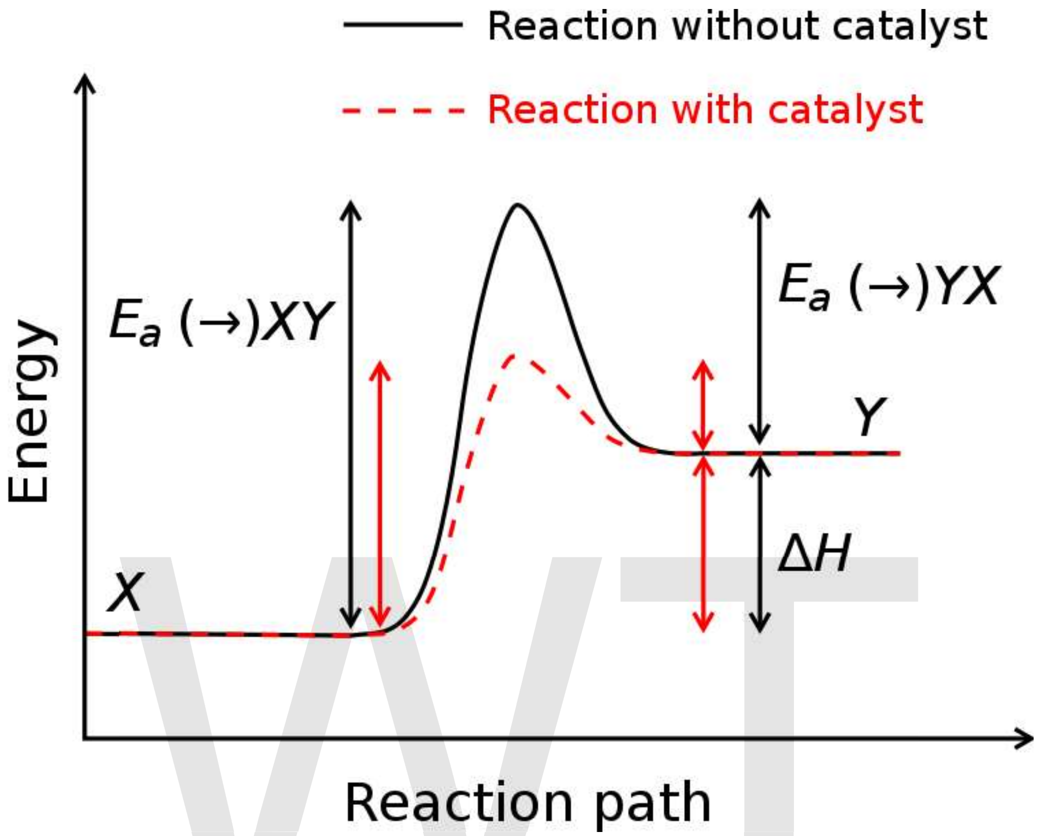


In this Paterno–Büchi reaction, a photoexcited carbonyl group is added to an unexcited olefin, yielding an oxetane.

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.

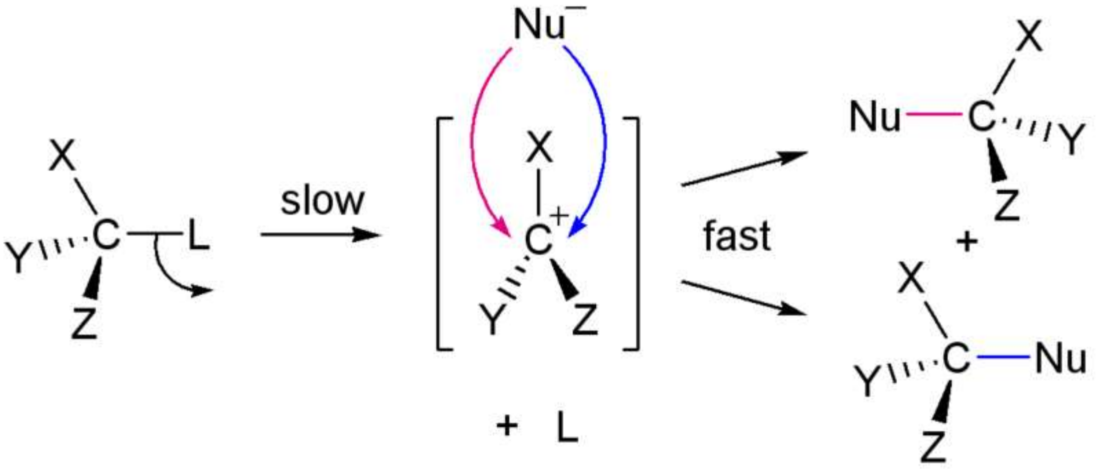
Reactions in organic chemistry

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.

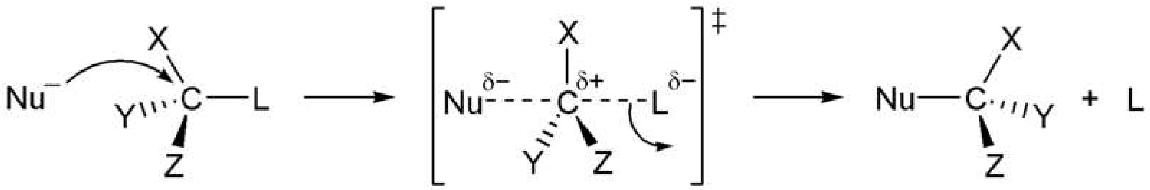
Substitution

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.

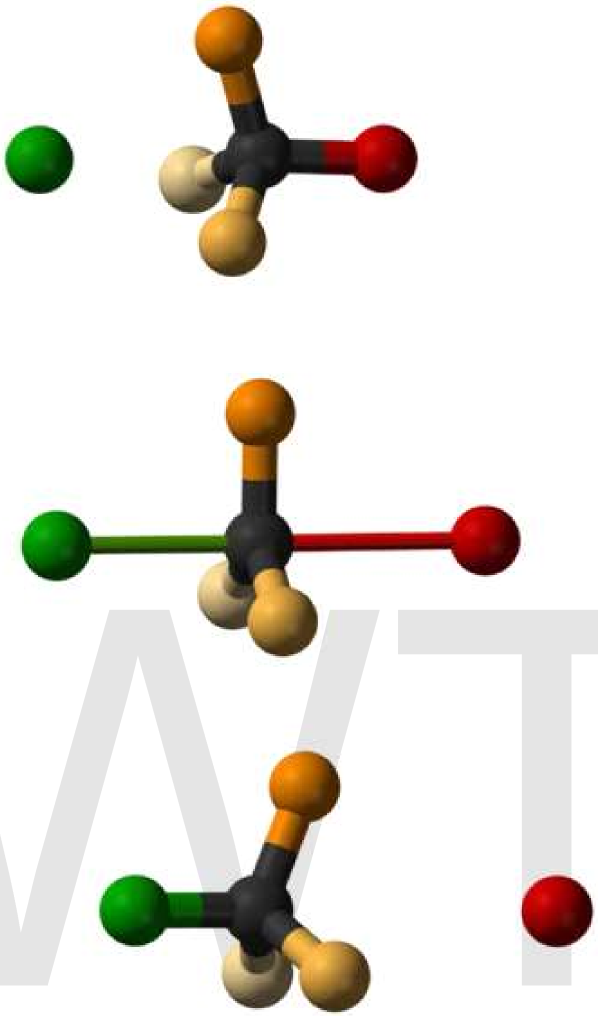
In the first type, a nucleophile, an atom or molecule with an excess of electrons and thus a negative charge or partial charge, replaces another atom or part of the "substrate" molecule. The electron pair from the nucleophile attacks the substrate forming a new bond, while the leaving group departs with 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.



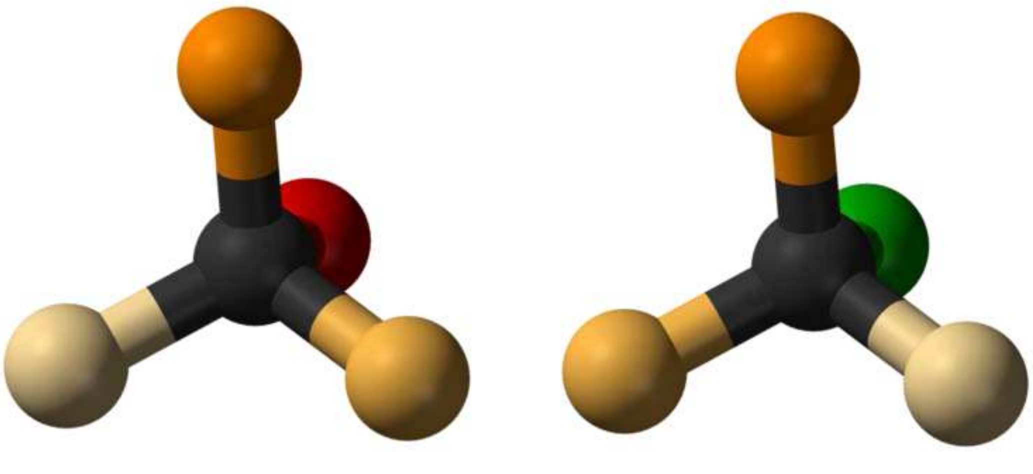
S_N1 mechanism



S_N2 mechanism



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

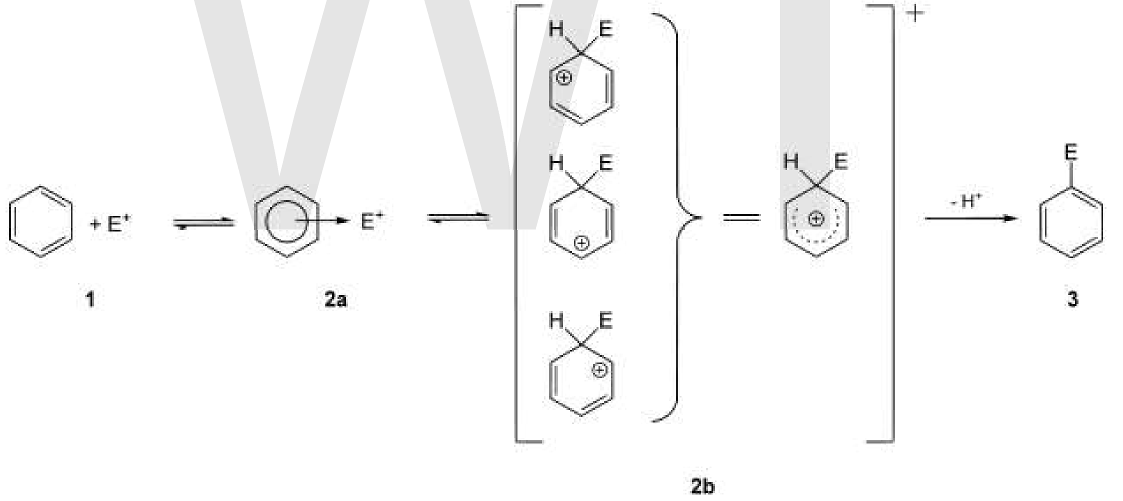


S_N2 reaction causes stereo inversion (Walden inversion)

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

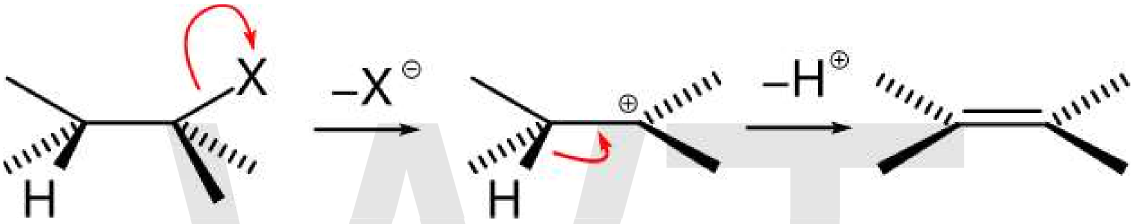
In the third type of substitution reaction, radical substitution, the attacking particle is a radical. This process usually takes the form of a chain reaction, for example in the reaction of alkanes with halogens. In the first step, light or heat disintegrates the halogen-containing molecules producing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

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

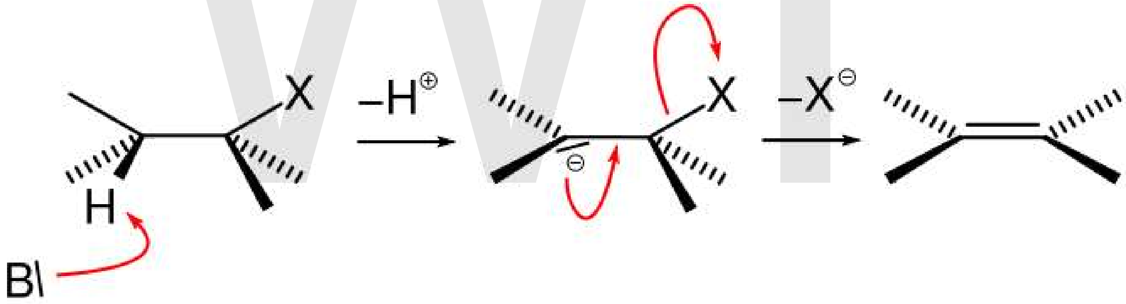
Reactions during the chain reaction of radical substitution

Addition and elimination

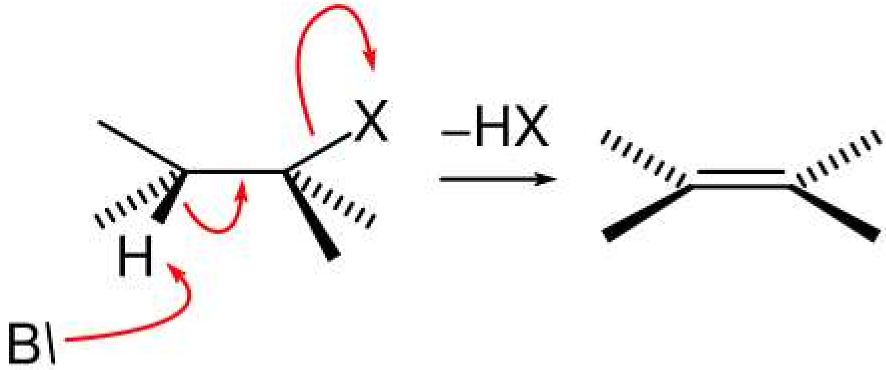
The addition and its counterpart, the elimination, are reactions which change the number of substituents on the carbon atom, and form or cleave multiple bonds. Double and triple bonds can be produced by eliminating a suitable leaving group. Similar to the nucleophilic substitution, there are several 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

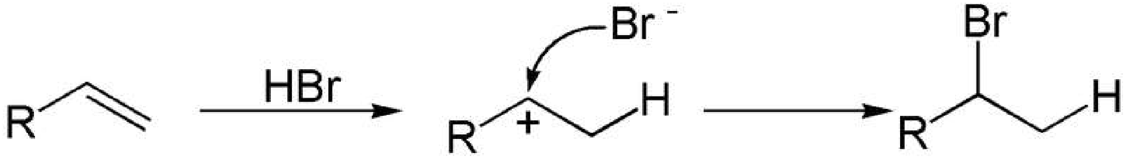


E1cb elimination



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.

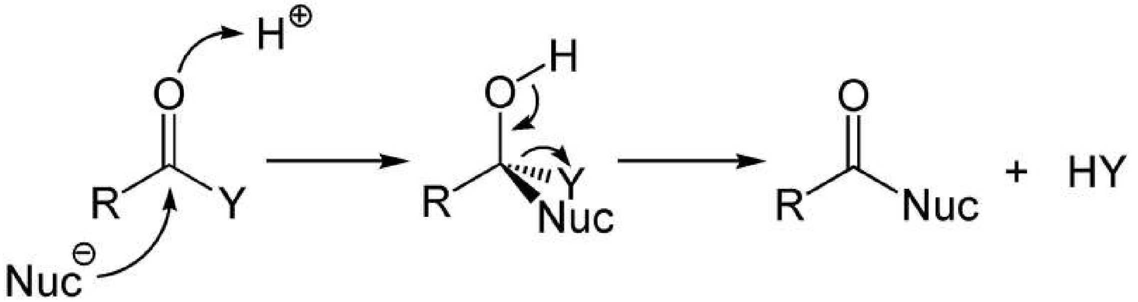


Electrophilic addition of hydrogen bromide

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.

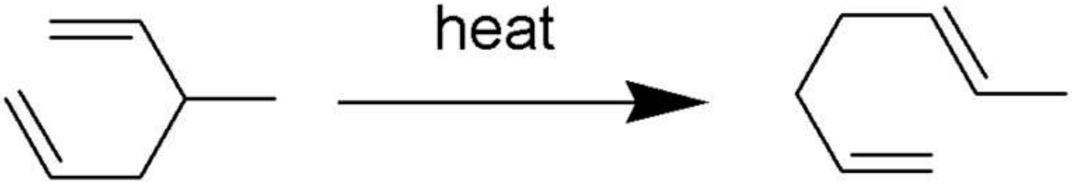


Acid-catalyzed addition-elimination mechanism

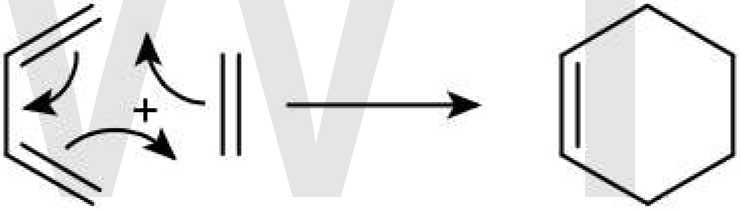
Nucleophilic addition of a carbanion or another nucleophile to the double bond of an alpha, beta unsaturated carbonyl compound can proceed via the Michael reaction, which belongs to the larger class of conjugate additions. This is one of the most useful methods for the mild formation of C-C bonds.

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.

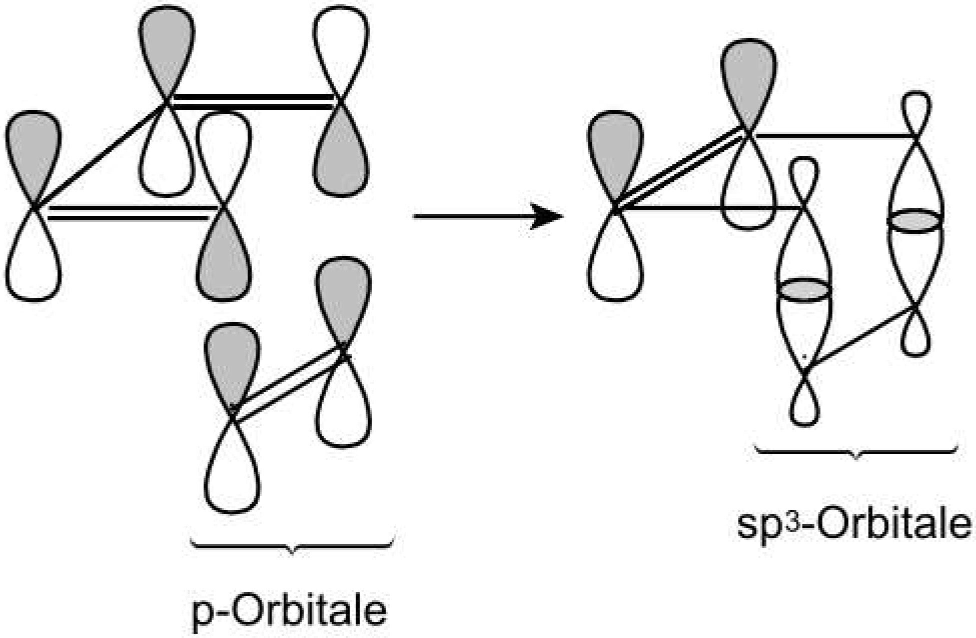
Other organic reaction mechanisms



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

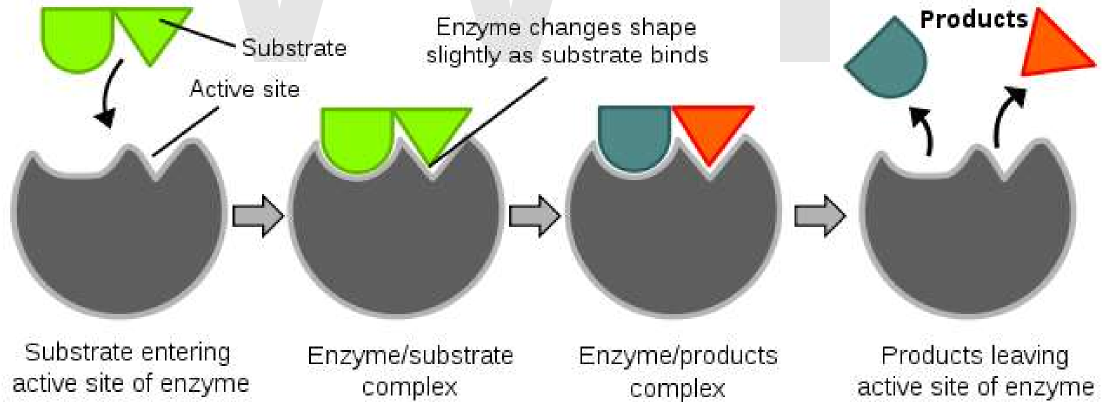


Illustration of the induced fit model of enzyme activity

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.

Chapter 9

Fluid Mechanics

Fluid mechanics is the study of fluids and the forces on them. (Fluids include liquids, gases, and plasmas.) Fluid mechanics can be divided into fluid kinematics, the study of fluid motion, and fluid dynamics, the study of the effect of forces on fluid motion, which can further be divided into fluid statics, the study of fluids at rest, and fluid kinetics, the study of fluids in motion. It is a branch of continuum mechanics, a subject which models matter without using the information that it is made out of atoms, that is, it models matter from a macroscopic viewpoint rather than from a microscopic viewpoint. Fluid mechanics, especially fluid dynamics, is an active field of research with many unsolved or partly solved problems. Fluid mechanics can be mathematically complex. Sometimes it can best be solved by numerical methods, typically using computers. A modern discipline, called computational fluid dynamics (CFD), is devoted to this approach to solving fluid mechanics problems. Also taking advantage of the highly visual nature of fluid flow is particle image velocimetry, an experimental method for visualizing and analyzing fluid flow.

Brief history

The study of fluid mechanics goes back at least to the days of ancient Greece, when Archimedes investigated fluid statics and buoyancy and formulated his famous law known now as the Archimedes Principle. Rapid advancement in fluid mechanics began with Leonardo da Vinci (observation and experiment), Evangelista Torricelli (barometer), Isaac Newton (viscosity) and Blaise Pascal (hydrostatics), and was continued by Daniel Bernoulli with the introduction of mathematical fluid dynamics in *Hydrodynamica* (1738). Inviscid flow was further analyzed by various mathematicians (Leonhard Euler, d'Alembert, Lagrange, Laplace, Poisson) and viscous flow was explored by a multitude of engineers including Poiseuille and Gotthilf Heinrich Ludwig Hagen. Further mathematical justification was provided by Claude-Louis Navier and George Gabriel Stokes in the Navier–Stokes equations, and boundary layers were investigated (Ludwig Prandtl), while various scientists (Osborne Reynolds, Andrey Kolmogorov, Geoffrey Ingram Taylor) advanced the understanding of fluid viscosity and turbulence.

Relationship to continuum mechanics

Fluid mechanics is a subdiscipline of continuum mechanics, as illustrated in the following table.

Continuum mechanics The study of the physics of continuous materials	Solid mechanics The study of the physics of continuous materials with a defined rest shape.	Elasticity Describes materials that return to their rest shape after an applied stress.	
		Plasticity Describes materials that permanently deform after a sufficient applied stress.	Rheology The study of materials with both solid and fluid characteristics.
	Fluid mechanics The study of the physics of continuous materials which take the shape of their container.	Non-Newtonian fluids	
		Newtonian fluids	

In a mechanical view, a fluid is a substance that does not support shear stress; that is why a fluid at rest has the shape of its containing vessel. A fluid at rest has no shear stress.

Assumptions

Like any mathematical model of the real world, fluid mechanics makes some basic assumptions about the materials being studied. These assumptions are turned into equations that must be satisfied if the assumptions are to be held true. For example, consider an incompressible fluid in three dimensions. The assumption that mass is conserved means that for any fixed closed surface (such as a sphere) the rate of mass passing from *outside* to *inside* the surface must be the same as rate of mass passing the other way. (Alternatively, the mass *inside* remains constant, as does the mass *outside*). This can be turned into an integral equation over the surface.

Fluid mechanics assumes that every fluid obeys the following:

- Conservation of mass
- Conservation of energy
- Conservation of momentum
- The *continuum hypothesis*, detailed below.

Further, it is often useful (at subsonic conditions) to assume a fluid is incompressible – that is, the density of the fluid does not change. Liquids can often be modelled as incompressible fluids, whereas gases cannot.

Similarly, it can sometimes be assumed that the viscosity of the fluid is zero (the fluid is *inviscid*). Gases can often be assumed to be inviscid. If a fluid is viscous, and its flow contained in some way (e.g. in a pipe), then the flow at the boundary must have zero velocity. For a viscous fluid, if the boundary is not porous, the shear forces between the fluid and the boundary results also in a zero velocity for the fluid at the boundary. This is called the no-slip condition. For a porous media otherwise, in the frontier of the containing vessel, the slip condition is not zero velocity, and the fluid has a discontinuous velocity field between the free fluid and the fluid in the porous media (this is related to the Beavers and Joseph condition).

The continuum hypothesis

Fluids are composed of molecules that collide with one another and solid objects. The continuum assumption, however, considers fluids to be continuous. That is, properties such as density, pressure, temperature, and velocity are taken to be well-defined at "infinitely" small points, defining a REV (Reference Element of Volume), at the geometric order of the distance between two adjacent molecules of fluid. Properties are assumed to vary continuously from one point to another, and are averaged values in the REV. The fact that the fluid is made up of discrete molecules is ignored.

The continuum hypothesis is basically an approximation, in the same way planets are approximated by point particles when dealing with celestial mechanics, and therefore results in approximate solutions. Consequently, assumption of the continuum hypothesis can lead to results which are not of desired accuracy. That said, under the right circumstances, the continuum hypothesis produces extremely accurate results.

Those problems for which the continuum hypothesis does not allow solutions of desired accuracy are solved using statistical mechanics. To determine whether or not to use conventional fluid dynamics or statistical mechanics, the Knudsen number is evaluated for the problem. The Knudsen number is defined as the ratio of the molecular mean free path length to a certain representative physical length scale. This length scale could be, for example, the radius of a body in a fluid. (More simply, the Knudsen number is how many times its own diameter a particle will travel on average before hitting another particle). Problems with Knudsen numbers at or above unity are best evaluated using statistical mechanics for reliable solutions.

Navier–Stokes equations

The **Navier–Stokes equations** (named after Claude-Louis Navier and George Gabriel Stokes) are the set of equations that describe the motion of fluid substances such as liquids and gases. These equations state that changes in momentum (force) of fluid particles depend only on the external pressure and internal viscous forces (similar to friction) acting on the fluid. Thus, the Navier–Stokes equations describe the balance of forces acting at any given region of the fluid.

The Navier–Stokes equations are differential equations which describe the motion of a fluid. Such equations establish relations among the rates of change of the variables of interest. For example, the Navier–Stokes equations for an ideal fluid with zero viscosity states that acceleration (the rate of change of velocity) is proportional to the derivative of internal pressure.

This means that solutions of the Navier–Stokes equations for a given physical problem must be sought with the help of calculus. In practical terms only the simplest cases can be solved exactly in this way. These cases generally involve non-turbulent, steady flow (flow does not change with time) in which the Reynolds number is small.

For more complex situations, such as global weather systems like El Niño or lift in a wing, solutions of the Navier–Stokes equations can currently only be found with the help of computers. This is a field of sciences by its own called computational fluid dynamics.

General form of the equation

The general form of the Navier–Stokes equations for the conservation of momentum is:

$$\rho\frac{D\mathbf{v}}{Dt} = \nabla\cdot\mathbb{P} + \rho\mathbf{f}$$

where

- ρ is the fluid density,
- $\frac{D}{Dt}$ is the substantive derivative (also called the material derivative),
- $\mathbf{v}$ is the velocity vector,
- $\mathbf{f}$ is the body force vector, and
- $\mathbb{P}$ is a tensor that represents the surface forces applied on a fluid particle (the stress tensor).

Unless the fluid is made up of spinning degrees of freedom like vortices, $\mathbb{P}$ is a symmetric tensor. In general, (in three dimensions) $\mathbb{P}$ has the form:

$$\mathbb{P} = \begin{pmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} \end{pmatrix}$$

where

- σ are normal stresses,
- τ are tangential stresses (shear stresses).

The above is actually a set of three equations, one per dimension. By themselves, these aren't sufficient to produce a solution. However, adding conservation of mass and appropriate boundary conditions to the system of equations produces a solvable set of equations.

Newtonian versus non-Newtonian fluids

A **Newtonian fluid** (named after Isaac Newton) is defined to be a fluid whose shear stress is linearly proportional to the velocity gradient in the direction perpendicular to the plane of shear. This definition means regardless of the forces acting on a fluid, it *continues to flow*. For example, water is a Newtonian fluid, because it continues to display fluid properties no matter how much it is stirred or mixed. A slightly less rigorous definition is that the drag of a small object being moved slowly through the fluid is proportional to the force applied to the object. (Compare friction). Important fluids, like water as well as most gases, behave — to good approximation — as a Newtonian fluid under normal conditions on Earth.

By contrast, stirring a non-Newtonian fluid can leave a "hole" behind. This will gradually fill up over time – this behaviour is seen in materials such as pudding, oobleck, or sand (although sand isn't strictly a fluid). Alternatively, stirring a non-Newtonian fluid can cause the viscosity to decrease, so the fluid appears "thinner" (this is seen in non-drip paints). There are many types of non-Newtonian fluids, as they are defined to be something that fails to obey a particular property — for example, most fluids with long molecular chains can react in a non-Newtonian manner.

Equations for a Newtonian fluid

The constant of proportionality between the shear stress and the velocity gradient is known as the viscosity. A simple equation to describe Newtonian fluid behaviour is

$$\tau = -\mu \frac{dv}{dy}$$

where

τ is the shear stress exerted by the fluid ("drag")
μ is the fluid viscosity – a constant of proportionality
$\frac{dv}{dy}$ is the velocity gradient perpendicular to the direction of shear.

For a Newtonian fluid, the viscosity, by definition, depends only on temperature and pressure, not on the forces acting upon it. If the fluid is incompressible and viscosity is constant across the fluid, the equation governing the shear stress (in Cartesian coordinates) is

$$\tau_{ij} = \mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)$$

where

τ_{ij} is the shear stress on the i^{th} face of a fluid element in the j^{th} direction
v_i is the velocity in the i^{th} direction
x_j is the j^{th} direction coordinate.

If a fluid does not obey this relation, it is termed a non-Newtonian fluid, of which there are several types.

Among fluids, two rough broad divisions can be made: ideal and non-ideal fluids. An ideal fluid really does not exist, but in some calculations, the assumption is justifiable. An Ideal fluid is non viscous- offers no resistance whatsoever to a shearing force.

One can group real fluids into Newtonian and non-Newtonian. Newtonian fluids agree with Newton's law of viscosity. Non-Newtonian fluids can be either plastic, bingham plastic, pseudoplastic, dilatant, thixotropic, rheopectic, viscoelatic.

Chapter 10

Heat Transfer

Heat transfer is a discipline of thermal engineering that concerns the transfer of thermal energy from one physical system to another. Heat transfer is classified into various mechanisms, such as heat conduction, convection, thermal radiation, and phase-change transfer. Engineers also consider the transfer of mass of differing chemical species, either cold or hot, to achieve heat transfer.

Conduction, also called diffusion, is the direct microscopic exchange of kinetic energy of particles through the boundary between two systems. When an object is at a different temperature from another body or its surroundings, heat flows so that the body and the surroundings reach the same temperature at thermal equilibrium. Such spontaneous heat transfer always occurs from a region of high temperature to another region of lower temperature, as required by the second law of thermodynamics.

Transfer by thermal radiation is the transfer of energy by transmission of electromagnetic radiation described by black body theory.

Overview

Heat is defined in physics as the transfer of thermal energy across a well-defined boundary around a thermodynamic system. It is a characteristics of a process and is not statically contained in matter. In engineering contexts, however, the term *heat transfer* has acquired a specific usage, despite its literal redundancy of the characterization of transfer. In these contexts, *heat* is taken as synonymous to thermal energy. This usage has its origin in the historical interpretation of heat as a fluid (*caloric*) that can be transferred by various causes, and that is also common in the language of laymen and everyday life.

Fundamental methods of heat transfer in engineering include conduction, convection, and radiation. Physical laws describe the behavior and characteristics of each of these methods. Real systems often exhibit a complicated combination of them. Heat transfer methods are used in numerous disciplines, such as automotive engineering, thermal management of electronic devices and systems, climate control, insulation, materials processing, and power plant engineering.

Various mathematical methods have been developed to solve or approximate the results of heat transfer in systems. Heat transfer is a path function (or process quantity), as opposed to a state quantity; therefore, the amount of heat transferred in a thermodynamic process that changes the state of a system depends on how that process occurs, not only the net difference between the initial and final states of the process. Heat flux is a quantitative, vectorial representation of the heat flow through a surface.

Heat transfer is typically studied as part of a general chemical engineering or mechanical engineering curriculum. Typically, thermodynamics is a prerequisite for heat transfer courses, as the laws of thermodynamics are essential to the mechanism of heat transfer. Other courses related to heat transfer include energy conversion, thermofluids, and mass transfer.

The transport equations for thermal energy (Fourier's law), mechanical momentum (Newton's law for fluids), and mass transfer (Fick's laws of diffusion) are similar and analogies among these three transport processes have been developed to facilitate prediction of conversion from any one to the others.

Mechanisms

The fundamental modes of heat transfer are:

Conduction or diffusion
    The transfer of energy between objects that are in physical contact
Convection
    The transfer of energy between an object and its environment, due to fluid motion
Radiation
    The transfer of energy to or from a body by means of the emission or absorption of electromagnetic radiation
Mass transfer
    The transfer of energy from one location to another as a side effect of physically moving an object containing that energy

Conduction

On a microscopic scale, heat conduction occurs as hot, rapidly moving or vibrating atoms and molecules interact with neighboring atoms and molecules, transferring some of their energy (heat) to these neighboring particles. In other words, heat is transferred by conduction when adjacent atoms vibrate against one another, or as electrons move from one atom to another. Conduction is the most significant means of heat transfer within a solid or between solid objects in thermal contact. Fluids—especially gases—are less conductive. Thermal contact conductance is the study of heat conduction between solid bodies in contact.

Steady state conduction is a form of conduction that happens when the temperature difference driving the conduction is constant, so that after an equilibration time, the spatial distribution of temperatures in the conducting object does not change any further. In steady state conduction, the amount of heat entering a section is equal to amount of heat coming out.

Transient conduction occurs when the temperature within an object changes as a function of time. Analysis of transient systems is more complex and often calls for the application of approximation theories or numerical analysis by computer.

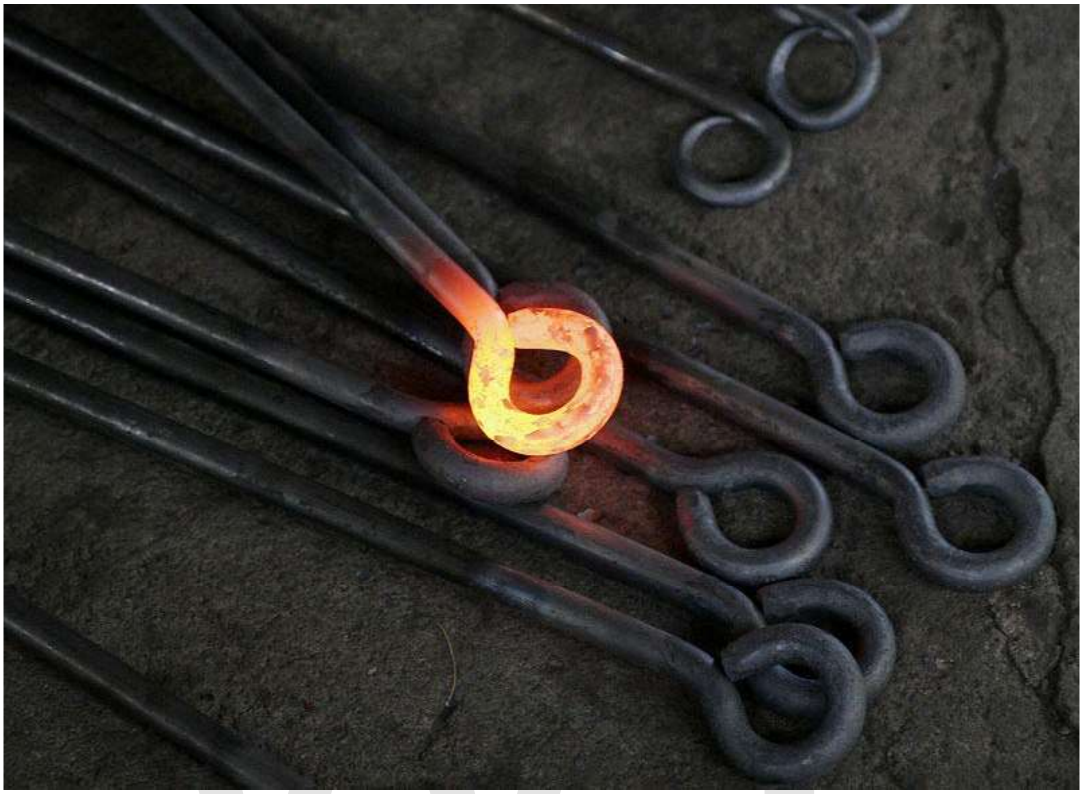
Convection

Convective heat transfer, or convection, is the transfer of heat from one place to another by the movement of fluids. (In physics, the term *fluid* means any substance that deforms under shear stress; it includes liquids, gases, plasmas, and some plastic solids.) Bulk motion of the fluid enhances the heat transfer between the solid surface and the fluid. Convection is usually the dominant form of heat transfer in liquids and gases. Although often discussed as a third method of heat transfer, convection actually describes the combined effects of conduction and fluid flow.

Free, or natural, convection occurs when the fluid motion is caused by buoyancy forces that result from density variations due to variations of temperature in the fluid. *Forced* convection is when the fluid is forced to flow over the surface by external means—such as fans, stirrers, and pumps—creating an artificially induced convection current.

Convection is described by Newton's law of cooling: "The rate of heat loss of a body is proportional to the difference in temperatures between the body and its surroundings."

Radiation



A red-hot iron object, transferring heat to the surrounding environment primarily through thermal radiation.

Thermal radiation is energy emitted by matter as electromagnetic waves due to the pool of thermal energy that all matter possesses that has a temperature above absolute zero. Thermal radiation propagates without the presence of matter through the vacuum of space.

Thermal radiation is a direct result of the random movements of atoms and molecules in matter. Since these atoms and molecules are composed of charged particles (protons and electrons), their movement results in the emission of electromagnetic radiation, which carries energy away from the surface.

Unlike conductive and convective forms of heat transfer, thermal radiation can be concentrated in a small spot by using reflecting mirrors, which is exploited in concentrating solar power generation. For example, the sunlight reflected from mirrors heats the PS10 solar power tower and during the day it can heat water to 285 °C (545 °F).

Mass Transfer

In mass transfer, energy—including thermal energy—is moved by the physical transfer of a hot or cold object from one place to another. This can be as simple as placing hot water in a bottle and heating a bed, or the movement of an iceberg in changing ocean currents. A practical example is thermal hydraulics.

Convection vs. conduction

In a body of fluid that is heated from underneath its container, conduction and convection can be considered to compete for dominance. If heat conduction is too great, fluid moving down by convection is heated by conduction so fast that its downward movement will be stopped due to its buoyancy, while fluid moving up by convection is cooled by conduction so fast that its driving buoyancy will diminish. On the other hand, if heat conduction is very low, a large temperature gradient may be formed and convection might be very strong.

The Rayleigh number (*Ra*) is a measure determining the result of this competition.

$$Ra = \frac{g\Delta\rho L^3}{\mu\alpha} = \frac{g\beta\Delta T L^3}{\nu\alpha}$$

where

- g is acceleration due to gravity
- ρ is the density with $\Delta\rho$ being the density difference between the lower and upper ends
- μ is the dynamic viscosity
- α is the Thermal diffusivity
- β is the volume thermal expansivity (sometimes denoted α elsewhere)
- T is the temperature and
- ν is the kinematic viscosity.

The Rayleigh number can be understood as the ratio between the rate of heat transfer by convection to the rate of heat transfer by conduction; or, equivalently, the ratio between the corresponding timescales (i.e. conduction timescale divided by convection timescale), up to a numerical factor. This can be seen as follows, where all calculations are up to numerical factors depending on the geometry of the system.

The buoyancy force driving the convection is roughly $g\Delta\rho L^3$, so the corresponding pressure is roughly $g\Delta\rho L$. In steady state, this is canceled by the shear stress due to viscosity, and therefore roughly equals $\mu V / L = \mu / T_{conv}$, where V is the typical fluid velocity due to convection and T_{conv} the order of its timescale. The conduction timescale, on the other hand, is of the order of $T_{cond} = L^2 / \alpha$.

Convection occurs when the Rayleigh number is above 1,000–2,000. For example, the Earth's mantle, exhibiting non-stable convection, has Rayleigh number of the order of 1,000, and T_{conv} as calculated above is around 100 million years.

Phase changes

Transfer of heat through a phase transition in the medium—such as water-to-ice, water-to-steam, steam-to-water, or ice-to-water—involves significant energy and is exploited in many ways: steam engines, refrigerators, etc. For example, the Mason equation is an approximate analytical expression for the growth of a water droplet based on the effects of heat transport on evaporation and condensation.

Boiling

Heat transfer in boiling fluids is complex, but of considerable technical importance. It is characterized by an *S*-shaped curve relating heat flux to surface temperature difference.

At low driving temperatures, no boiling occurs and the heat transfer rate is controlled by the usual single-phase mechanisms. As the surface temperature is increased, local boiling occurs and vapor bubbles nucleate, grow into the surrounding cooler fluid, and collapse. This is *sub-cooled nucleate boiling*, and is a very efficient heat transfer mechanism. At high bubble generation rates, the bubbles begin to interfere and the heat flux no longer increases rapidly with surface temperature (this is the departure from nucleate boiling, or DNB). At higher temperatures still, a maximum in the heat flux is reached (the critical heat flux, or CHF). The regime of falling heat transfer that follows is not easy to study, but is believed to be characterized by alternate periods of nucleate and film boiling. Nucleate boiling slows the heat transfer due to gas bubbles on the heater's surface; as mentioned, gas-phase thermal conductivity is much lower than liquid-phase thermal conductivity, so the outcome is a kind of "gas thermal barrier".

At higher temperatures still, the hydrodynamically-quieter regime of film boiling is reached. Heat fluxes across the stable vapor layers are low, but rise slowly with temperature. Any contact between fluid and the surface that may be seen probably leads to the extremely rapid nucleation of a fresh vapor layer ("spontaneous nucleation").

Condensation

Condensation occurs when a vapor is cooled and changes its phase to a liquid. Condensation heat transfer, like boiling, is of great significance in industry. During condensation, the latent heat of vaporization must be released. The amount of the heat is the same as that absorbed during vaporization at the same fluid pressure.

There are several types of condensation:

- Homogeneous condensation, as during a formation of fog.
- Condensation in direct contact with subcooled liquid.
- Condensation on direct contact with a cooling wall of a heat exchanger: This is the most common mode used in industry:
  - Filmwise condensation is when a liquid film is formed on the subcooled surface, and usually occurs when the liquid wets the surface.
  - Dropwise condensation is when liquid drops are formed on the subcooled surface, and usually occurs when the liquid does not wet the surface.

  Dropwise condensation is difficult to sustain reliably; therefore, industrial equipment is normally designed to operate in filmwise condensation mode.

Modeling approaches

Complex heat transfer phenomena can be modeled in different ways.

Heat equation

The heat equation is an important partial differential equation that describes the distribution of heat (or variation in temperature) in a given region over time. In some cases, exact solutions of the equation are available; in other cases the equation must be solved numerically using computational methods. For example, simplified climate models may use Newtonian cooling, instead of a full (and computationally expensive) radiation code, to maintain atmospheric temperatures.

Lumped system analysis

System analysis by the lumped capacitance model is a common approximation in transient conduction that may be used whenever heat conduction within an object is much faster than heat conduction across the boundary of the object.

This is a method of approximation that reduces one aspect of the transient conduction system—that within the object—to an equivalent steady state system. That is, the method assumes that the temperature within the object is completely uniform, although its value may be changing in time.

In this method, the ratio of the conductive heat resistance within the object to the convective heat transfer resistance across the object's boundary, known as the *Biot number*, is calculated. For small Biot numbers, the approximation of *spatially uniform temperature within the object* can be used: it can be presumed that heat transferred into the object has time to uniformly distribute itself, due to the lower resistance to doing so, as compared with the resistance to heat entering the object.

Applications and techniques

Heat transfer has broad application to the functioning of numerous devices and systems. Heat-transfer principles may be used to preserve, increase, or decrease temperature in a wide variety of circumstances.

Insulation and radiant barriers

Heat exposure as part of a fire test for firestop products.

Thermal insulators are materials specifically designed to reduce the flow of heat by limiting conduction, convection, or both. Radiant barriers are materials that reflect radiation, and therefore reduce the flow of heat from radiation sources. Good insulators are not necessarily good radiant barriers, and vice versa. Metal, for instance, is an excellent reflector and a poor insulator.

The effectiveness of an insulator is indicated by its **R-value**, or resistance value. The R-value of a material is the inverse of the conduction coefficient (*k*) multiplied by the thickness (*d*) of the insulator. In most of the world, R-values are measured in SI units: square-meter kelvins per watt ($m^2 \cdot K/W$). In the United States, R-values are customarily given in units of British thermal units per hour per square-foot degrees Fahrenheit ($Btu/h \cdot ft^2 \cdot °F$).

$$R = \frac{d}{k}$$

$$C = \frac{Q}{m \Delta T}$$

Rigid fiberglass, a common insulation material, has an R-value of four per inch, while poured concrete, a poor insulator, has an R-value of 0.08 per inch.

The tog is a measure of thermal resistance, commonly used in the textile industry, and often seen quoted on, for example, duvets and carpet underlay.

The effectiveness of a radiant barrier is indicated by its **reflectivity**, which is the fraction of radiation reflected. A material with a high reflectivity (at a given wavelength) has a low emissivity (at that same wavelength), and vice versa. At any specific wavelength, reflectivity = 1 - emissivity. An ideal radiant barrier would have a reflectivity of 1, and would therefore reflect 100 percent of incoming radiation. Vacuum flasks, or Dewars, are silvered to approach this ideal. In the vacuum of space, satellites use multi-layer insulation, which consists of many layers of aluminized (shiny) Mylar to greatly reduce radiation heat transfer and control satellite temperature.

Critical insulation thickness

Low thermal conductivity (*k*) materials reduce heat fluxes. The smaller the *k* value, the larger the corresponding thermal resistance (*R*) value. Thermal conductivity is measured in watts-per-meter per kelvin ($W \cdot m^{-1} \cdot K^{-1}$), represented as *k*. As the thickness of insulating material increases, the thermal resistance—or R-value—also increases.

However, adding layers of insulation has the potential of increasing the surface area, and hence the thermal convection area.

For example, as thicker insulation is added to a cylindrical pipe, the outer radius of the pipe-and-insulation system increases, and therefore surface area increases. The point where the added resistance of increasing insulation thickness becomes overshadowed by the effect of increased surface area is called the critical insulation thickness. In simple cylindrical pipes, this is calculated as a radius:

$$R_{critical} = \frac{k}{h}$$

Heat exchangers

A heat exchanger is a tool built for efficient heat transfer from one fluid to another, whether the fluids are separated by a solid wall so that they never mix, or the fluids are in direct contact. Heat exchangers are widely used in refrigeration, air conditioning, space heating, power generation, and chemical processing. One common example of a heat exchanger is a car's radiator, in which the hot coolant fluid is cooled by the flow of air over the radiator's surface.

Common types of heat exchanger flows include parallel flow, counter flow, and cross flow. In parallel flow, both fluids move in the same direction while transferring heat; in counter flow, the fluids move in opposite directions; and in cross flow, the fluids move at right angles to each other. Common constructions for heat exchanger include shell and tube, double pipe, extruded finned pipe, spiral fin pipe, u-tube, and stacked plate.

When engineers calculate the theoretical heat transfer in a heat exchanger, they must contend with the fact that the driving temperature difference between the two fluids varies with position. To account for this in simple systems, the log mean temperature difference (LMTD) is often used as an "average" temperature. In more complex systems, direct knowledge of the LMTD is not available, and the number of transfer units (NTU) method can be used instead.

Heat dissipation

A heat sink is a component that transfers heat generated within a solid material to a fluid medium, such as air or a liquid. Examples of heat sinks are the heat exchangers used in refrigeration and air conditioning systems, and the radiator in a car (which is also a heat exchanger). Heat sinks also help to cool electronic and optoelectronic devices such as CPUs, higher-power lasers, and light-emitting diodes (LEDs). A heat sink uses its extended surfaces to increase the surface area in contact with the cooling fluid.

Buildings

In cold climates, houses with their heating systems form dissipative systems. In spite of efforts to insulate houses to reduce heat losses via their exteriors, considerable heat is lost, which can make their interiors uncomfortably cool or cold. For the comfort of the inhabitants, the interiors must be maintained out of thermal equilibrium with the external surroundings. In effect, these domestic residences are oases of warmth in a sea of cold, and the thermal gradient between the inside and outside is often quite steep. This can lead to problems such as condensation and uncomfortable air currents, which—if left unaddressed—can cause cosmetic or structural damage to the property. Such issues can be prevented by use of insulation techniques for reducing heat loss.

Thermal transmittance is the rate of transfer of heat through a structure divided by the difference in temperature across the structure. It is expressed in watts per square meter per kelvin, or W/m^2K. Well-insulated parts of a building have a low thermal transmittance, whereas poorly-insulated parts of a building have a high thermal transmittance.

A thermostat is a device capable of starting the heating system when the house's interior falls below a set temperature, and of stopping that same system when another (higher) set temperature has been achieved. Thus, the thermostat controls the flow of energy into the house, that energy eventually being dissipated to the exterior.

Thermal energy storage

Thermal energy storage refers to technologies that store energy in a thermal reservoir for later use. They can be employed to balance energy demand between daytime and nighttime. The thermal reservoir may be maintained at a temperature above (hotter) or below (colder) than that of the ambient environment. Applications include later use in space heating, domestic or process hot water, or to generate electricity. Most practical active solar heating systems have storage for a few hours to a day's worth of heat collected.

Evaporative cooling

Evaporative cooling is a physical phenomenon in which evaporation of a liquid, typically into surrounding air, cools an object or a liquid in contact with it. Latent heat describes the amount of heat that is needed to evaporate the liquid; this heat comes from the liquid itself and the surrounding gas and surfaces. The greater the difference between the two temperatures, the greater the evaporative cooling effect. When the temperatures are the same, no net evaporation of water in air occurs; thus, there is no cooling effect. A simple example of natural evaporative cooling is perspiration, or sweat, which the body secretes in order to cool itself. An evaporative cooler is a device that cools air through the simple evaporation of water.

Radiative cooling

Radiative cooling is the process by which a body loses heat by radiation. It is an important effect in the Earth's atmosphere. In the case of the Earth-atmosphere system, it refers to the process by which long-wave (infrared) radiation is emitted to balance the absorption of short-wave (visible) energy from the Sun. Convective transport of heat and evaporative transport of latent heat both remove heat from the surface and redistribute it in the atmosphere, making it available for radiative transport at higher altitudes.

Laser cooling

Laser cooling refers to techniques in which atomic and molecular samples are cooled through the interaction with one or more laser light fields. The most common method of laser cooling is Doppler cooling. In Doppler cooling, the frequency of the laser light is tuned slightly below an electronic transition in the atom. Thus, the atoms would absorb more photons if they moved towards the light source, due to the Doppler effect. If an excited atom then emits a photon spontaneously, it will be accelerated. The result of the absorption and emission process is to reduce the speed of the atom. Eventually the mean velocity, and therefore the kinetic energy of the atoms, will be reduced. Since the temperature of an ensemble of atoms is a measure of the random internal kinetic energy, this is equivalent to cooling the atoms.

Sympathetic cooling is a process in which particles of one type cool particles of another type. Typically, atomic ions that can be directly laser-cooled are used to cool nearby ions or atoms. This technique allows cooling of ions and atoms that cannot be laser cooled directly.

Magnetic cooling

Magnetic evaporative cooling is a technique for lowering the temperature of a group of atoms. The process confines atoms using a magnetic field. Over time, individual atoms will become much more energetic than the others due to random collisions, and will escape—removing energy from the system and reducing the temperature of the remaining group. This process is similar to the familiar process by which standing water becomes water vapor.

Other

A heat pipe is a passive device constructed in such a way that it acts as though it has extremely high thermal conductivity. Heat pipes use latent heat and capillary action to move heat, and can carry many times as much heat as a similar-sized copper rod. Originally invented for use in satellites, they have applications in personal computers.

A thermocouple is a junction between two different metals that produces a voltage related to a temperature difference. Thermocouples are a widely used type of temperature sensor for measurement and control, and can also be used to convert heat into electric power.

A thermopile is an electronic device that converts thermal energy into electrical energy. It is composed of thermocouples. Thermopiles do not measure the absolute temperature, but generate an output voltage proportional to a temperature difference. Thermopiles are widely used, e.g., they are the key component of infrared thermometers, such as those used to measure body temperature via the ear.

A thermal diode or thermal rectifier is a device that preferentially passes heat in one direction: a "one-way valve" for heat.

Chapter 11

Mass Transfer and Process Design

Mass Transfer

Mass transfer is the net movement of mass from one location to another. Mass transfer is used by different scientific disciplines for different processes and mechanisms. The phrase is commonly used in engineering for physical processes that involve molecular and convective transport of atoms and molecules within physical systems.

Some common examples of mass transfer processes are the evaporation of water from a pond to the atmosphere; the diffusion of chemical impurities in lakes, rivers, and oceans from natural or artificial point sources; separation of chemical components in distillation columns. In Cooling towers, hot water flows down over the fill material as air flows up and contact between water and air evaporates some of the water. Evaporation requires heat; the heat is removed from the remaining water lowering its temperature.

Astrophysics

In astrophysics, mass transfer is the process by which matter gravitationally bound to a body, usually a star, fills its Roche lobe and becomes gravitationally bound to a second body, usually a compact object (white dwarf, neutron star or black hole), and is eventually accreted onto it. It is a common phenomenon in binary systems, and may play an important role in some types of supernovae and pulsars.

Chemical Engineering

Mass transfer finds extensive application in chemical engineering problems. Often, chemical species transfer between two phases through an interface or diffusion through a phase. The driving force for mass transfer is a difference in concentration; the random motion of molecules causes a net transfer of mass from an area of high concentration to an area of low concentration. For separation processes, thermodynamics determines the extent of separation, while mass transfer determines the rate at which the separation will occur. The amount of mass transfer rate can be quantified through the calculation and application of mass transfer coefficients.

Analogies between heat, mass, and momentum transfer

There are some notable similarities in equations for momentum, heat, and mass transfer. The molecular transfer equations of Newton's law for fluid momentum, Fourier's law for heat, and Fick's law for mass are very similar. A great deal of effort has been devoted to developing analogies among these three transport processes so as to allow prediction of one from any of the others.

Process Design

Process design is the design of processes for desired physical and/or chemical transformation of materials. Process design is central to chemical engineering and it can be considered to be the summit of chemical engineering, bringing together all of the components of that field.

Process design can be the design of new facilities or it can be the modification or expansion of existing facilities. The design starts at a conceptual level and ultimately ends in the form of fabrication and construction plans.

Process design is distinct from equipment design, which is closer in spirit to the design of unit operations. Processes often include many unit operations.

Documentation

Process design documents serve to define the design and they ensure that the design components fit together. They are useful in communicating ideas and plans to other engineers involved with the design, to external regulatory agencies, to equipment vendors and to construction contractors.

In order of increasing detail, process design documents include:

- **Block Flow Diagrams (BFD)**: Very simple diagrams composed of rectangles and lines indicating major material or energy flows.
- **Process Flow Diagrams (PFD's)**: Typically more complex diagrams of major unit operations as well as flow lines. They usually include a material balance, and sometimes an energy balance, showing typical or design flowrates, stream compositions, and stream and equipment pressures and temperatures.
- **Piping and Instrumentation Diagrams (P&ID's)**: Diagrams showing each and every pipeline with piping class (carbon steel or stainless steel) and pipe size (diameter). They also show valving along with instrument locations and process control schemes.
- **Specifications**: Written design requirements of all major equipment items.

Process designers also typically write operating manuals on how to start-up, operate and shut-down the process.

Documents are maintained after construction of the process facility for the operating personnel to refer to. The documents also are useful when modifications to the facility are planned.

A primary method of developing the process documents is process flowsheeting.

Design Considerations

Designs have objectives and constraints, and even a simple process requires a trade-off among such factors.

Objectives that a design may strive to include:

- Throughput rate
- Process yield
- Product purity

Constraints include:

- Capital cost
- Available space
- Safety concerns
- Environmental impact and projected effluents and emissions
- Waste production
- Operating and maintenance costs

Other factors that designers may include are:

- Reliability
- Redundancy
- Flexibility
- Anticipated variability in feedstock and allowable variability in product.

Sources of Design Information

Designers usually do not start from scratch, especially for complex projects. Often the engineers have pilot plant data available or data from full-scale operating facilities. Other sources of information include proprietary design criteria provided by process licensors, published scientific data, laboratory experiments, and input.

Computer Help

The advent of low cost powerful computers has aided complex mathematical simulation of processes, and simulation software is often used by design engineers. Simulations can identify weaknesses in designs and allow engineers to choose better alternatives.

However, engineers still rely on heuristics, intuition, and experience when designing a process. Human creativity is an element in complex designs.

Chapter 12

Electrostatic Precipitator

Electrostatic precipitator of a biomass heating system with a heat power of 2 MW

An **electrostatic precipitator** (ESP), or **electrostatic air cleaner** is a particulate collection device that removes particles from a flowing gas (such as air) using the force of an induced electrostatic charge. Electrostatic precipitators are highly efficient filtration devices that minimally impede the flow of gases through the device, and can easily remove fine particulate matter such as dust and smoke from the air stream. In contrast to wet scrubbers which apply energy directly to the flowing fluid medium, an ESP applies energy only to the particulate matter being collected and therefore is very efficient in its consumption of energy (in the form of electricity).

Invention of the electrostatic precipitator

The first use of corona discharge to remove particles from an aerosol was by Hohlfeld in 1824. However, it was not commercialized until almost a century later. In 1907 Dr. Frederick G. Cottrell applied for a patent on a device for charging particles and then collecting them through electrostatic attraction — the first electrostatic precipitator. He was then a professor of chemistry at the University of California, Berkeley. Cottrell first applied the device to the collection of sulfuric acid mist and lead oxide fume emitted from various acid-making and smelting activities. Vineyards in northern California were being adversely affected by the lead emissions.

At the time of Cottrell's invention, the theoretical basis for operation was not understood. The operational theory was developed later in the 1920s, in Germany.

Prof. Cottrell used proceeds from his invention to fund scientific research through the creation of a foundation called Research Corporation in 1912 to which he assigned the patents. The intent of the organization was to bring inventions made by educators (such as Cottrell) into the commercial world for the benefit of society at large. The operation of Research Corporation is perpetuated by royalties paid by commercial firms after commercialization occurs. Research Corporation has provided vital funding to many scientific projects: Goddard's rocketry experiments, Lawrence's cyclotron, production methods for vitamins A and B_1, among many others. By a decision of the U.S. Supreme Court the Corporation had to be split into two entities, the Research Corporation and two commercial firms making the hardware: Research-Cottrell Inc. (operating east of the Mississippi River) and Western Precipitation operating in the Western states. The Research Corporation continues to be active to this day and the two companies formed to commercialize the invention for industrial and utility applications are still in business as well.

Electrophoresis is the term used for migration of gas-suspended charged particles in a direct-current electrostatic field. If your television set accumulates dust on the face it is because of this phenomenon (a CRT is a direct-current machine operating at about 35kV).

The plate precipitator

The most basic precipitator contains a row of thin vertical wires, and followed by a stack of large flat metal plates oriented vertically, with the plates typically spaced about 1 cm to 18 cm apart, depending on the application. The air or gas stream flows horizontally through the spaces between the wires, and then passes through the stack of plates.

A negative voltage of several thousand volts is applied between wire and plate. If the applied voltage is high enough an electric (corona) discharge ionizes the gas around the electrodes. Negative ions flow to the plates and charge the gas-flow particles.

The ionized particles, following the negative electric field created by the power supply, move to the grounded plates.

Particles build up on the collection plates and form a layer. The layer does not collapse, thanks to electrostatic pressure (given from layer resistivity, electric field, and current flowing in the collected layer).

Collection efficiency (*R*)

Precipitator performance is very sensitive due to two particulate properties: 1) Resistivity; and 2) Particle size distribution. These properties can be determined economically and accurately in the laboratory. A widely taught concept to calculate the collection efficiency is the Deutsch model, which assumes infinite remixing of the particles perpendicular to the gas stream.

Resistivity can be determined as a function of temperature in accordance with IEEE Standard 548. This test is conducted in an air environment containing a specified moisture concentration. The test is run as a function of ascending or descending temperature or both. Data are acquired using an average ash layer electric field of 4 kV/cm. Since relatively low applied voltage is used and no sulfuric acid vapor is present in the environment, the values obtained indicate the maximum ash resistivity.

Usually the descending temperature test is suggested when no unusual circumstances are involved. Before the test, the ash is thermally equilibrated in dry air at 454 °C (850°F) for about 14 hours. It is believed that this procedure anneals the ash and restores the surface to pre-collection condition.

If there is a concern about the effect of combustibles, the residual effect of a conditioning agent other than sulfuric acid vapor, or the effect of some other agent that inhibits the reaction of the ash with water vapor, the combination of the ascending and descending test mode is recommended. The thermal treatment that occurs between the two test modes is capable of eliminating the foregoing effects. This results in ascending and descending temperature resistivity curves that show a hysteresis related to the presence and removal of some effect such as a significant level of combustibles.

With particles of high resistivity (cement dust for example) Sulfur trioxide is sometimes injected into a flue gas stream to lower the resistivity of the particles in order to improve the collection efficiency of the electrostatic precipitator.

Modern industrial electrostatic precipitators

ESPs continue to be excellent devices for control of many industrial particulate emissions, including smoke from electricity-generating utilities (coal and oil fired), salt cake collection from black liquor boilers in pulp mills, and catalyst collection from fluidized bed catalytic cracker units in oil refineries to name a few. These devices treat gas volumes from several hundred thousand ACFM to 2.5 million ACFM (1,180 m^3/s) in the largest coal-fired boiler applications. For a coal-fired boiler the collection is usually performed downstream of the air preheater at about 160 °C (320 deg.F) which provides optimal resistivity of the coal-ash particles. For some difficult applications with low-sulfur fuel hot-end units have been built operating above 371 °C (700 deg.F).

The original parallel plate–weighted wire design (described above) has evolved as more efficient (and robust) discharge electrode designs were developed, today focusing on rigid (pipe-frame) discharge electrodes to which many sharpened spikes are attached (barbed wire), maximizing corona production. Transformer-rectifier systems apply voltages of 50 – 100 kV at relatively high current densities. Modern controls, such as an automatic voltage control, minimize sparking and prevent arcing (sparks are quenched within 1/2 cycle of the TR set), avoiding damage to the components. Automatic plate-rapping systems and hopper-evacuation systems remove the collected particulate matter while on line, theoretically allowing ESPs to stay in operation for years at a time.

Wet electrostatic precipitator

A wet electrostatic precipitator (WESP or wet ESP) operates with saturated air streams (100% relative humidity). WESPs are commonly used to remove liquid droplets such as sulfuric acid mist from industrial process gas streams. The WESP is also commonly used where the gases are high in moisture content, contain combustible particulate, have particles that are sticky in nature.

The preferred and most modern type of WESP is a downflow tubular design. This design allows the collected moisture and particulate to form a slurry that helps to keep the collection surfaces clean.

Plate style and upflow design WESPs are very unreliable and should not be used in applications where particulate is sticky in nature.

Consumer-oriented electrostatic air cleaners

Plate precipitators are commonly marketed to the public as air purifier devices or as a permanent replacement for furnace filters, but all have the undesirable attribute of being somewhat messy to clean. A negative side-effect of electrostatic precipitation devices is the production of toxic ozone and NO_x. However, electrostatic precipitators offer benefits over other air purifications technologies, such as HEPA filtration, which require expensive filters and can become "production sinks" for many harmful forms of bacteria.

The two-stage design (charging section ahead of collecting section) has the benefit of minimizing ozone production which would adversely affect health of personnel working in enclosed spaces. For shipboard engine rooms where gearboxes generate an oil fog, two-stage ESP's are used to clean the air improving the operating environment and preventing buildup of flammable oil fog accumulations. Collected oil is returned to the gear lubricating system.

With electrostatic precipitators, if the collection plates are allowed to accumulate large amounts of particulate matter, the particles can sometimes bond so tightly to the metal plates that vigorous washing and scrubbing may be required to completely clean the collection plates. The close spacing of the plates can make thorough cleaning difficult, and the stack of plates often cannot be easily disassembled for cleaning. One solution, suggested by several manufacturers, is to wash the collector plates in a dishwasher.

Some consumer precipitation filters are sold with special soak-off cleaners, where the entire plate array is removed from the precipitator and soaked in a large container overnight, to help loosen the tightly bonded particulates.

A study by the Canada Mortgage and Housing Corporation testing a variety of forced-air furnace filters found that ESP filters provided the best, and most cost-effective means of cleaning air using a forced-air system.

Chapter 13

Electroplating

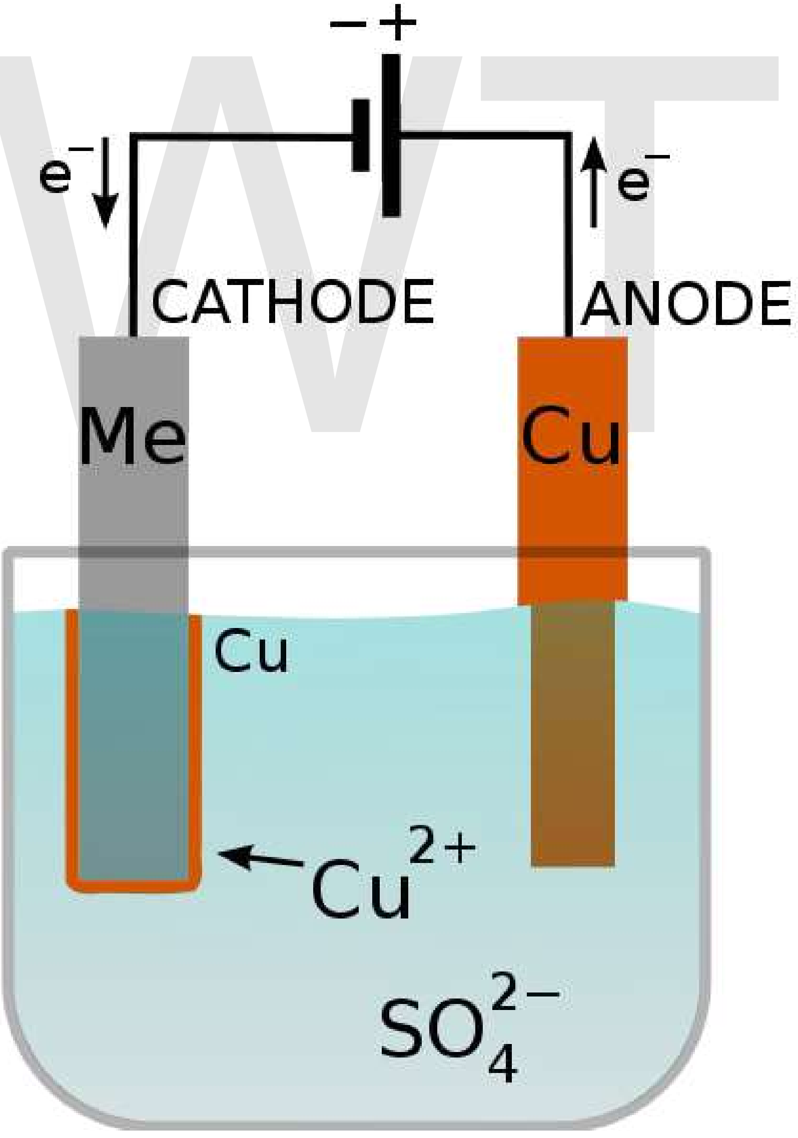
copper electroplating machine for layering PCBs

Electroplating is a plating process in which metal ions in a solution are moved by an electric field to coat an electrode. The process uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal. Electroplating is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities, etc.) to a surface that otherwise lacks that property. Another application uses electroplating to build up thickness on undersized parts.

The process used in electroplating is called **electrodeposition**. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A power supply supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they "plate out" onto the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, vis-a-vis the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode.

Other electroplating processes may use a nonconsumable anode such as lead. In these techniques, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution.

Process



Electroplating of a metal (Me) with copper in a copper sulfate bath.

The anode and cathode in the electroplating cell are both connected to an external supply of direct current - a battery or, more commonly, a rectifier. The anode is connected to the positive terminal of the supply, and the cathode (article to be plated) is connected to the negative terminal. When the external power supply is switched on, the metal at the anode is oxidized from the zero valence state to form cations with a positive charge. These cations associate with the anions in the solution. The cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, in an acid solution, copper is oxidized at the anode to Cu^{2+} by losing two electrons. The Cu^{2+} associates with the anion SO_4^{2-} in the solution to form copper sulfate. At the cathode, the Cu^{2+} is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder.

Many plating baths include cyanides of other metals (e.g., potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity. Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity.

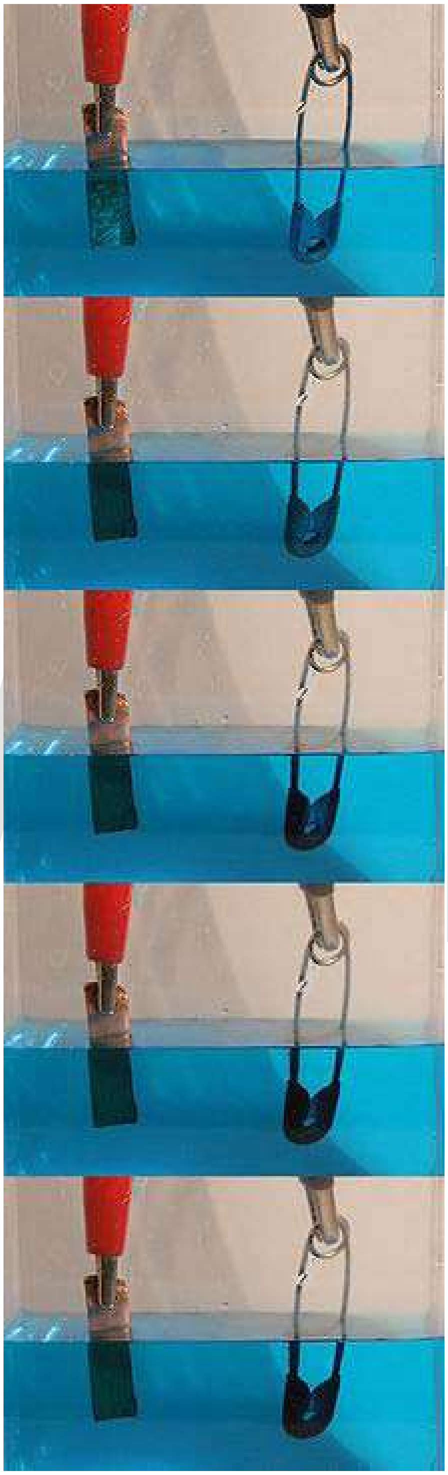
When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes.

Strike

Initially, a special plating deposit called a "strike" or "flash" may be used to form a very thin (typically less than 0.1 micrometer thick) plating with high quality and good adherence to the substrate. This serves as a foundation for subsequent plating processes. A strike uses a high current density and a bath with a low ion concentration. The process is slow, so more efficient plating processes are used once the desired strike thickness is obtained.

The striking method is also used in combination with the plating of different metals. If it is desirable to plate one type of deposit onto a metal to improve corrosion resistance but this metal has inherently poor adhesion to the substrate, a strike can be first deposited that is compatible with both. One example of this situation is the poor adhesion of electrolytic nickel on zinc alloys, in which case a copper strike is used, which has good adherence to both.

Current density



A timecourse of electroplating with copper. The anode on the left is pure copper, the safety pin on the right is the target for plating. The first image is before the electrical supply has been connected, the second image shows plating with a thin layer of copper and the later images show the buildup of "fluffy" structurally weak deposits.

The current density (current of the electroplating current divided by the surface area of the part) in this process strongly influences the deposition rate, plating adherence, and plating quality. This density can vary over the surface of a part, as outside surfaces will tend to have a higher current density than inside surfaces (e.g., holes, bores, etc.). The higher the current density, the faster the deposition rate will be, although there is a practical limit enforced by poor adhesion and plating quality when the deposition rate is too high.

While most plating cells use a continuous direct current, some employ a cycle of 8–15 seconds on followed by 1–3 seconds off. This technique is commonly referred to as "pulse plating" and allows high current densities to be used while still producing a quality deposit. In order to deal with the uneven plating rates that result from high current densities, the current is even sometimes reversed in a method known as "pulse-reverse plating", causing some of the plating from the thicker sections to re-enter the solution. In effect, this allows the "valleys" to be filled without over-plating the "peaks". This is common on rough parts or when a bright finish is required. In a typical pulse reverse operation, the reverse current density is three times greater than the forward current density and the reverse pulse width is less than one-quarter the forward pulse width. Pulse-reverse processes can be operated at a wide range of frequencies from several hundred hertz up to the order of megahertz.

Brush electroplating

A closely-related process is brush electroplating, in which localized areas or entire items are plated using a brush saturated with plating solution. The brush, typically a stainless steel body wrapped with a cloth material that both holds the plating solution and prevents direct contact with the item being plated, is connected to the positive side of a low voltage direct-current power source, and the item to be plated connected to the negative. The operator dips the brush in plating solution then applies it to the item, moving the brush continually to get an even distribution of the plating material. The brush acts as the anode, but typically does not contribute any plating material, although sometimes the brush is made from or contains the plating material in order to extend the life of the plating solution.

Brush electroplating has several advantages over tank plating, including portability, ability to plate items that for some reason cannot be tank plated (one application was the plating of portions of very large decorative support columns in a building restoration), low or no masking requirements, and comparatively low plating solution volume requirements. Disadvantages compared to tank plating can include greater operator involvement (tank plating can frequently be done with minimal attention), and inability to achieve as great a plate thickness.

Electroless deposition

Usually an electrolytic cell (consisting of two electrodes, electrolyte, and external source of current) is used for electrodeposition. In contrast, an electroless deposition process uses only one electrode and no external source of electric current. However, the solution for the electroless process needs to contain a reducing agent so that the electrode reaction has the form:

$$M^{z+} + Red_{solution} \overset{\text{catalytic surface}}{\Longrightarrow} M_{solid} + Oxy_{solution}$$

In principle any water-based reducer can be used although the redox potential of the reducer half-cell must be high enough to overcome the energy barriers inherent in liquid chemistry. Electroless nickel plating uses hypophosphite as the reducer while plating of other metals like silver, gold and copper typically use low molecular weight aldehydes.

A major benefit of this approach over electroplating is that power sources and plating baths are not needed, reducing the cost of production. The technique can also plate diverse shapes and types of surface. The downside is that the plating process is usually slower and cannot create such thick plates of metal. As a consequence of these characteristics, electroless deposition is quite common in the decorative arts.

Cleanliness

Cleanliness is essential to successful electroplating, since molecular layers of oil can prevent adhesion of the coating. ASTM B322 is a standard guide for cleaning metals prior to electroplating. Cleaning processes include solvent cleaning, hot alkaline detergent cleaning, electrocleaning, and acid etc. The most common industrial test for cleanliness is the waterbreak test, in which the surface is thoroughly rinsed and held vertical. Hydrophobic contaminants such as oils cause the water to bead and break up, allowing the water to drain rapidly. Perfectly clean metal surfaces are hydrophilic and will retain an unbroken sheet of water that does not bead up or drain off. ASTM F22 describes a version of this test. This test does not detect hydrophilic contaminants, but the electroplating process can displace these easily since the solutions are water-based. Surfactants such as soap reduce the sensitivity of the test and must be thoroughly rinsed off.

Effects

Electroplating changes the chemical, physical, and mechanical properties of the workpiece. An example of a chemical change is when nickel plating improves corrosion resistance. An example of a physical change is a change in the outward appearance. An example of a mechanical change is a change in tensile strength or surface hardness.

Limitations

Obtaining a uniform thickness with electroplating can be difficult depending on the geometry of the object being plated. The plating metal is preferentially attracted to external corners and protrusions, but unattracted to internal corners and recesses. These difficulties can be overcome with multiple anodes or a specially shaped anode that mimics the object geometry, however both of these solutions increase cost. The ability of a plating to cover uniformly is called *throwing power*; the better the "throwing power" the more uniform the coating.

One cannot electroplate chrome or silver on any given substrate directly. Many plating processes require an intermediate plating step. For example, when chrome plating carbon steel, one would need to electroplate copper on top of carbon steel, followed by nickel and then chrome to get uniform chrome plated part. These additional steps add considerably to the cost and time to electroplate. Thicker coatings require similar multilayer structures. A hard chrome coating would require multiple alternating coatings of copper and chrome.

History

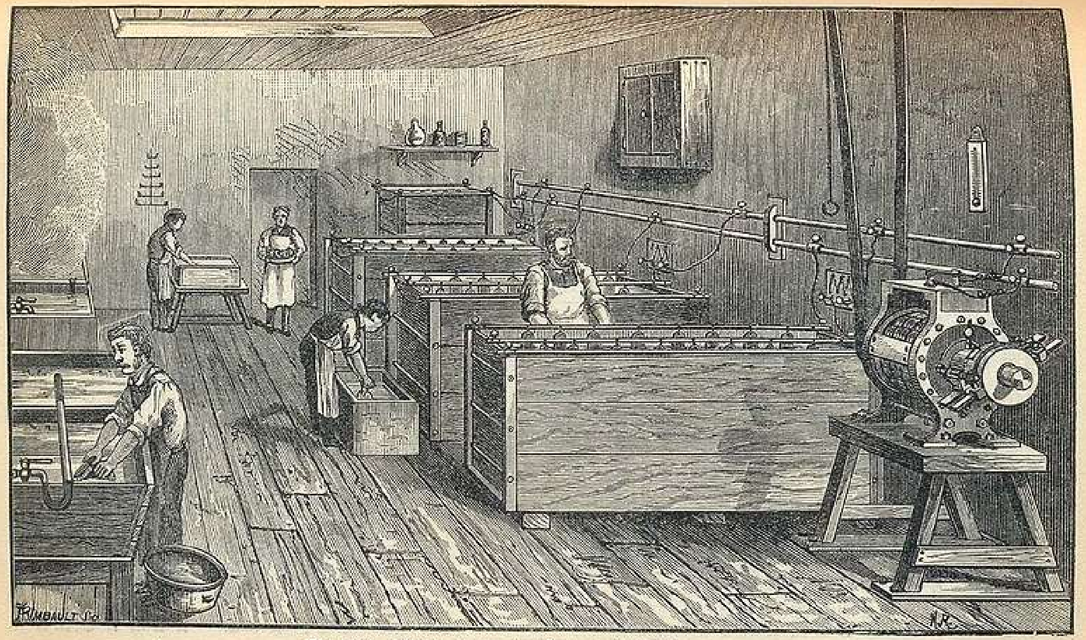


Fig. 108.—Nickel-plating by Dynamo-electricity.

Nickel plating

Although it is not confirmed, the Parthian Battery may have been the first system used for electroplating.

Modern electrochemistry was invented by Italian chemist Luigi V. Brugnatelli in 1805. Brugnatelli used his colleague Alessandro Volta's invention of five years earlier, the voltaic pile, to facilitate the first electrodeposition. Brugnatelli's inventions were suppressed by the French Academy of Sciences and did not become used in general industry for the following thirty years.

By 1839, scientists in Britain and Russia had independently devised metal deposition processes similar to Brugnatelli's for the copper electroplating of printing press plates. Soon after, John Wright of Birmingham, England discovered that potassium cyanide was a suitable electrolyte for gold and silver electroplating. Wright's associates, George Elkington and Henry Elkington were awarded the first patents for electroplating in 1840. These two then founded the electroplating industry in Birmingham from where it spread around the world.

The Norddeutsche Affinerie in Hamburg was the first modern electroplating plant starting its production in 1876.

As the science of electrochemistry grew, its relationship to the electroplating process became understood and other types of non-decorative metal electroplating processes were developed. Commercial electroplating of nickel, brass, tin, and zinc were developed by the 1850s. Electroplating baths and equipment based on the patents of the Elkingtons were scaled up to accommodate the plating of numerous large scale objects and for specific manufacturing and engineering applications.

The plating industry received a big boost from the advent of the development of electric generators in the late 19th century. With the higher currents, available metal machine components, hardware, and automotive parts requiring corrosion protection and enhanced wear properties, along with better appearance, could be processed in bulk.

The two World Wars and the growing aviation industry gave impetus to further developments and refinements including such processes as hard chromium plating, bronze alloy plating, sulfamate nickel plating, along with numerous other plating processes. Plating equipment evolved from manually operated tar-lined wooden tanks to automated equipment, capable of processing thousands of kilograms per hour of parts.

One of the American physicist Richard Feynman's first projects was to develop technology for electroplating metal onto plastic. Feynman developed the original idea of his friend into a successful invention, allowing his employer (and friend) to keep commercial promises he had made but could not have fulfilled otherwise.

Hull cell

A zinc solution tested in a hull cell

The *Hull cell* is a type of test cell used to qualitatively check the condition of a electroplating bath. It allows for optimization for current density range, optimization of additive concentration, recognition of impurity effects and indication of macro-throwing power capability. The Hull cell replicates the plating bath on a lab scale. It is filled with a sample of the plating solution, an appropriate anode which is connected to a rectifier. The "work" is replaced with a hull cell test panel that will be plated to show the "health" of the bath.

The Hull cell is a trapezoidal container that holds 267 ml of solution. This shape allows one to place the test panel on an angle to the anode. As a result, the deposit is plated at different current densities which can be measured with a hull cell ruler. The solution volume allows for a quantitative optimization of additive concentration: 1 gram addition to 267 mL is equivalent to 0.5 oz/gal in the plating tank.

Chapter 14

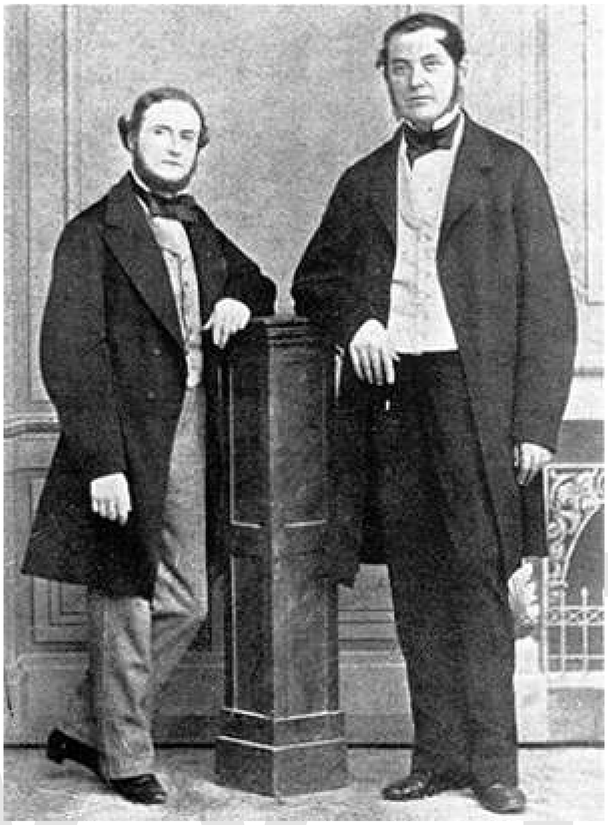
Analytical Chemistry

Analytical chemistry is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials. Qualitative analysis gives an indication of the identity of the chemical species in the sample and quantitative analysis determines the amount of one or more of these components. The separation of components is often performed prior to analysis.

Analytical methods can be separated into classical and instrumental. Classical methods (also known as wet chemistry methods) use separations such as precipitation, extraction, and distillation and qualitative analysis by color, odor, or melting point. Quantitative analysis is achieved by measurement of weight or volume. Instrumental methods use an apparatus to measure physical quantities of the analyte such as light absorption, fluorescence, or conductivity. The separation of materials is accomplished using chromatography or electrophoresis methods.

Analytical chemistry is also focused on improvements in experimental design, chemometrics, and the creation of new measurement tools to provide better chemical information. Analytical chemistry has applications in forensics, bioanalysis, clinical analysis, environmental analysis, and materials analysis.

History



Gustav Kirchhoff (left) and Robert Bunsen (right)

Analytical chemistry has been important since the early days of chemistry, providing methods for determining which elements and chemicals are present in the world around us. During this period significant analytical contributions to chemistry include the development of systematic elemental analysis by Justus von Liebig and systematized organic analysis based on the specific reactions of functional groups.

The first instrumental analysis was flame emissive spectrometry developed by Robert Bunsen and Gustav Kirchhoff who discovered rubidium (Rb) and caesium (Cs) in 1860.

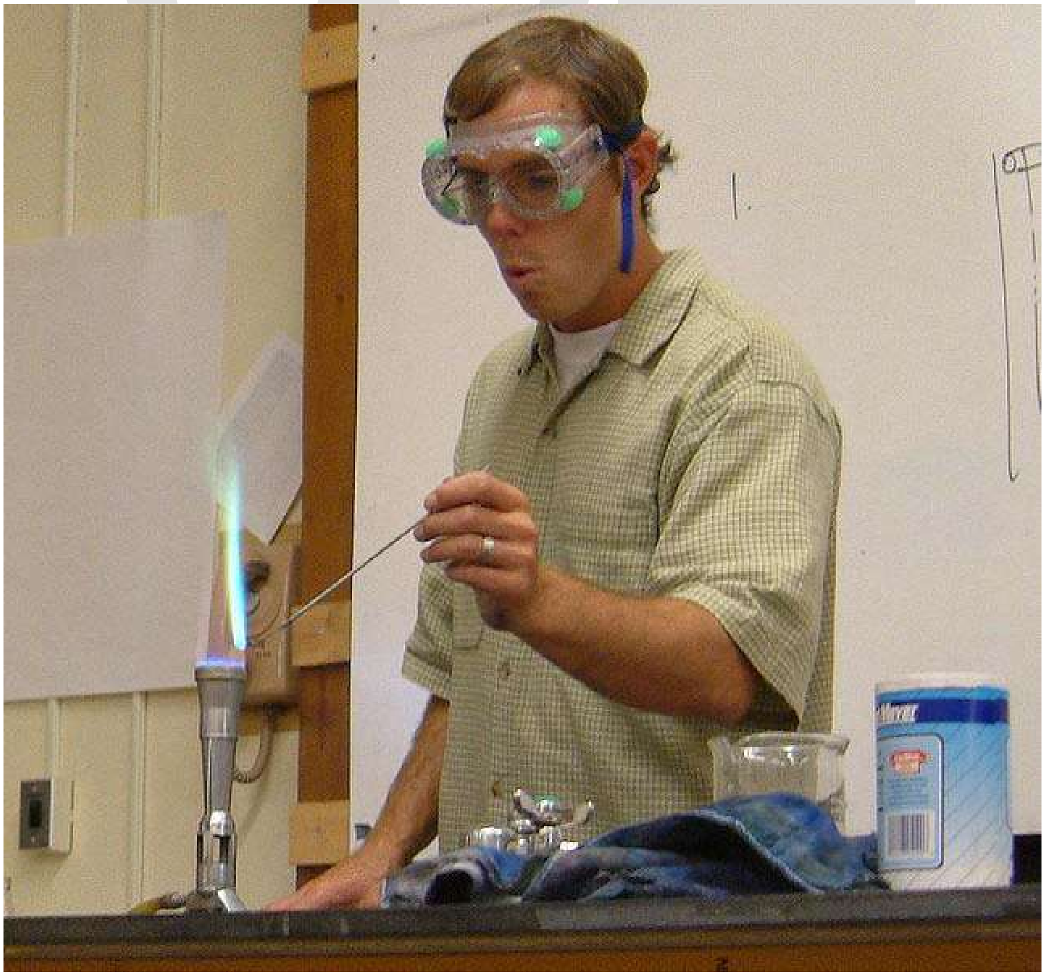
Most of the major developments in analytical chemistry take place after 1900. During this period instrumental analysis becomes progressively dominant in the field. In particular many of the basic spectroscopic and spectrometric techniques were discovered in the early 20th century and refined in the late 20th century.

The separation sciences follow a similar time line of development and also become increasingly transformed into high performance instruments. In the 1970s many of these techniques began to be used together to achieve a complete characterization of samples.

Starting in approximately the 1970s into the present day analytical chemistry has progressively become more inclusive of biological questions (bioanalytical chemistry), whereas it had previously been largely focused on inorganic or small organic molecules. Lasers have been increasingly used in chemistry as probes and even to start and influence a wide variety of reactions. The late 20th century also saw an expansion of the application of analytical chemistry from somewhat academic chemical questions to forensic, environmental, industrial and medical questions, such as in histology.

Modern analytical chemistry is dominated by instrumental analysis. Many analytical chemists focus on a single type of instrument. Academics tend to either focus on new applications and discoveries or on new methods of analysis. The discovery of a chemical present in blood that increases the risk of cancer would be a discovery that an analytical chemist might be involved in. An effort to develop a new method might involve the use of a tunable laser to increase the specificity and sensitivity of a spectrometric method. Many methods, once developed, are kept purposely static so that data can be compared over long periods of time. This is particularly true in industrial quality assurance (QA), forensic and environmental applications. Analytical chemistry plays an increasingly important role in the pharmaceutical industry where, aside from QA, it is used in discovery of new drug candidates and in clinical applications where understanding the interactions between the drug and the patient are critical.

Classical methods



The presence of copper in this qualitative analysis is indicated by the bluish-green color of the flame.

Although modern analytical chemistry is dominated by sophisticated instrumentation, the roots of analytical chemistry and some of the principles used in modern instruments are from traditional techniques many of which are still used today. These techniques also tend to form the backbone of most undergraduate analytical chemistry educational labs.

Qualitative analysis

A qualitative analysis determines the presence or absence of a particular compound, but not the mass or concentration. That is, it is not related to quantity.

Chemical tests

There are numerous qualitative chemical tests, for example, the acid test for gold and the Kastle-Meyer test for the presence of blood.

Flame test

Inorganic qualitative analysis generally refers to a systematic scheme to confirm the presence of certain, usually aqueous, ions or elements by performing a series of reactions that eliminate ranges of possibilities and then confirms suspected ions with a confirming test. Sometimes small carbon containing ions are included in such schemes. With modern instrumentation these tests are rarely used but can be useful for educational purposes and in field work or other situations where access to state-of-the-art instruments are not available or expedient.

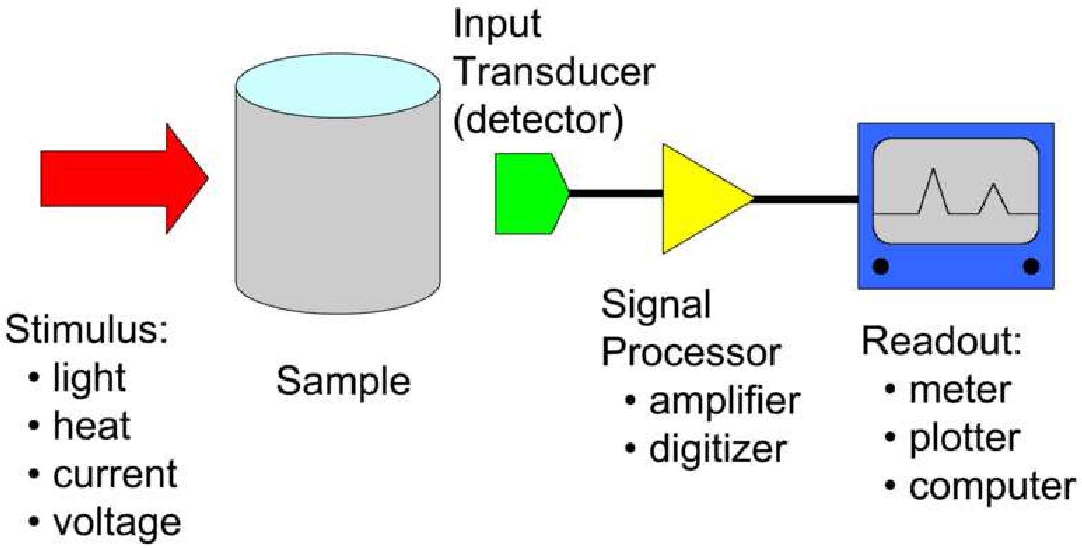
Gravimetric analysis

Gravimetric analysis involves determining the amount of material present by weighing the sample before and/or after some transformation. A common example used in undergraduate education is the determination of the amount of water in a hydrate by heating the sample to remove the water such that the difference in weight is due to the loss of water.

Volumetric analysis

Titration involves the addition of a reactant to a solution being analyzed until some equivalence point is reached. Often the amount of material in the solution being analyzed may be determined. Most familiar to those who have taken college chemistry is the acid-base titration involving a color changing indicator. There are many other types of titrations, for example potentiometric titrations. These titrations may use different types of indicators to reach some equivalence point.

Instrumental methods

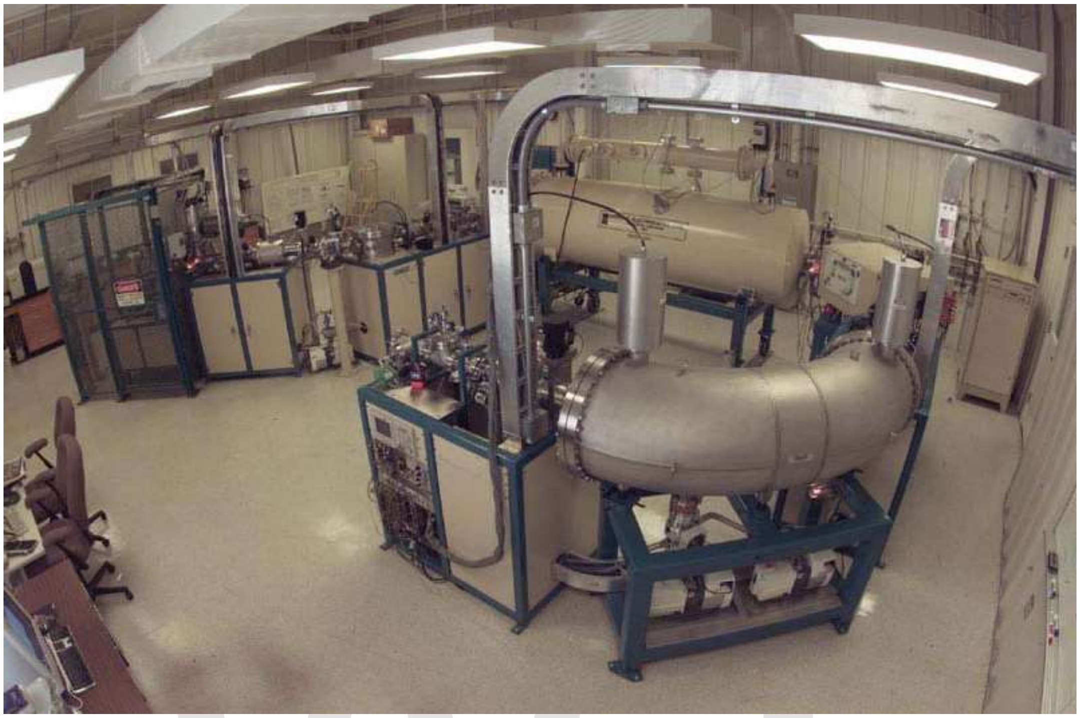


Block diagram of an analytical instrument showing the stimulus and measurement of response

Spectroscopy

Spectroscopy measures the interaction of the molecules with electromagnetic radiation. Spectroscopy consists of many different applications such as atomic absorption spectroscopy, atomic emission spectroscopy, ultraviolet-visible spectroscopy, x-ray fluorescence spectroscopy, infrared spectroscopy, Raman spectroscopy, dual polarisation interferometry, nuclear magnetic resonance spectroscopy, photoemission spectroscopy, Mössbauer spectroscopy and so on.

Mass spectrometry



An accelerator mass spectrometer used for radiocarbon dating and other analysis.

Mass spectrometry measures mass-to-charge ratio of molecules using electric and magnetic fields. There are several ionization methods: electron impact, chemical ionization, electrospray, fast atom bombardment, matrix assisted laser desorption ionization, and others. Also, mass spectrometry is categorized by approaches of mass analyzers: magnetic-sector, quadrupole mass analyzer, quadrupole ion trap, time-of-flight, Fourier transform ion cyclotron resonance, and so on.

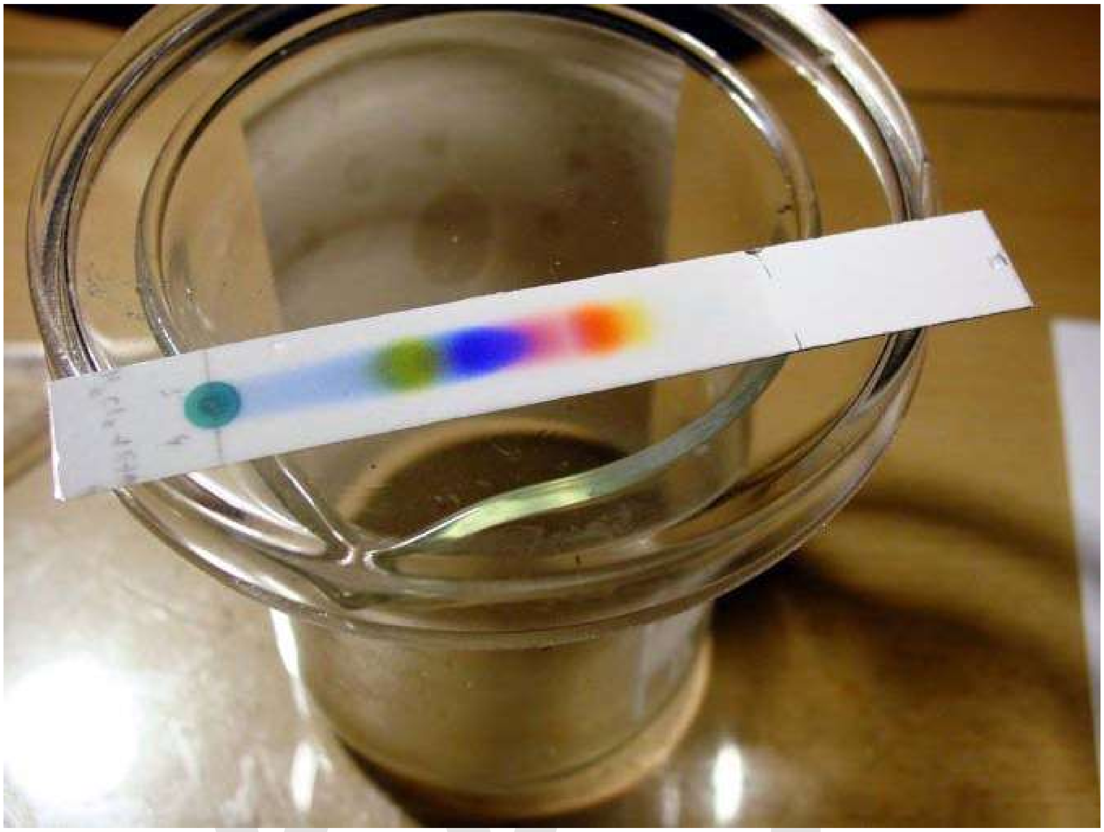
Electrochemical analysis

Electroanalytical methods measure the potential (volts) and/or current (amps) in an electrochemical cell containing the analyte. These methods can be categorized according to which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential).

Thermal analysis

Calorimetry and thermogravimetric analysis measure the interaction of a material and heat.

Separation



Separation of black ink on a thin layer chromatography plate.

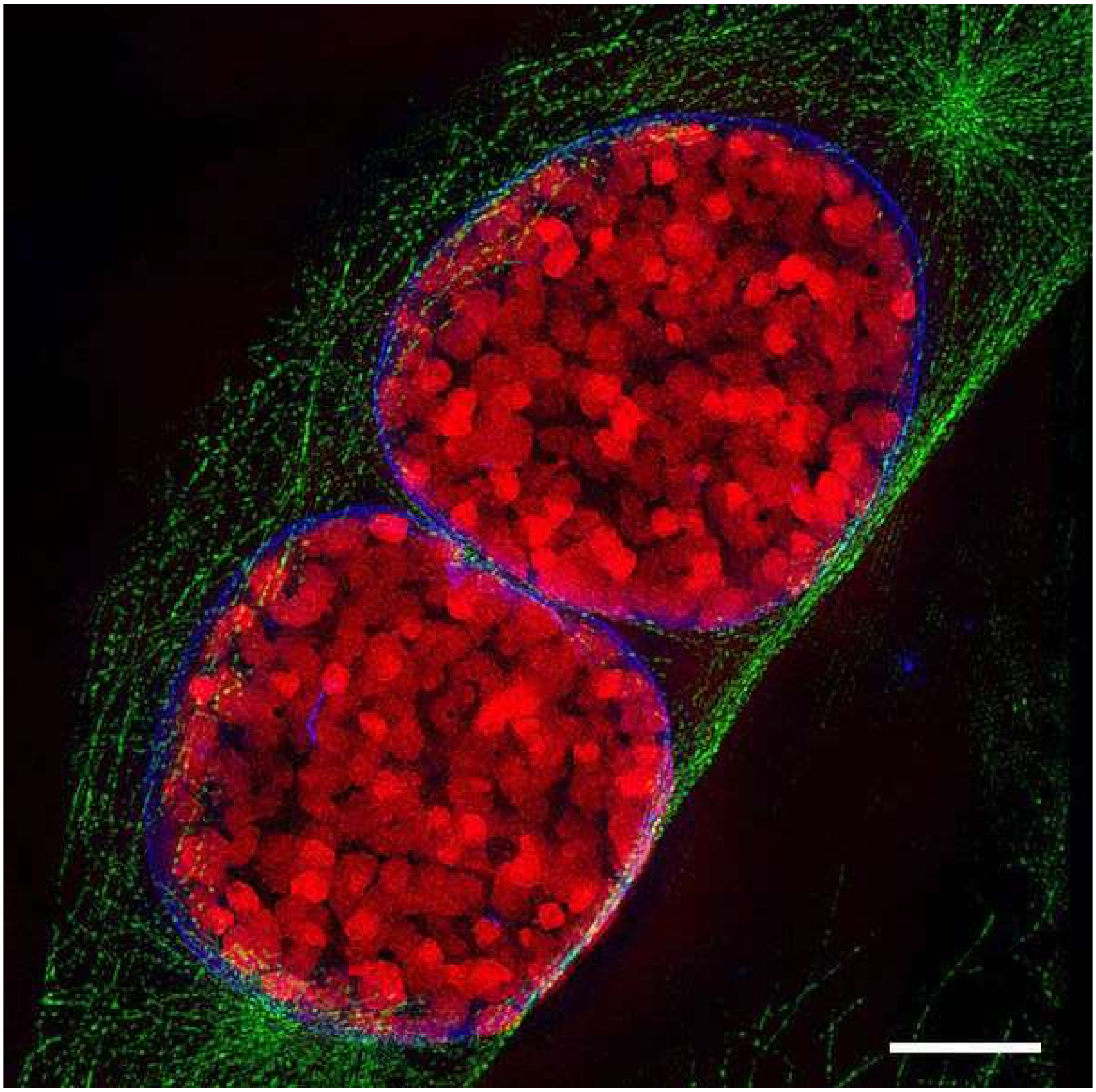
Separation processes are used to decrease the complexity of material mixtures. Chromatography and electrophoresis are representative of this field.

Hybrid techniques

Combinations of the above techniques produce a "hybrid" or "hyphenated" technique. Several examples are in popular use today and new hybrid techniques are under development. For example, gas chromatography-mass spectrometry, gas chromatography-infrared spectroscopy, liquid chromatography-mass spectrometry, liquid chromatography-NMR spectroscopy. liquid chromagraphy-infrared spectroscopy and capillary electrophoresis-mass spectrometry.

Hyphenated separation techniques refers to a combination of two (or more) techniques to detect and separate chemicals from solutions. Most often the other technique is some form of chromatography. Hyphenated techniques are widely used in chemistry and biochemistry. A slash is sometimes used instead of hyphen, especially if the name of one of the methods contains a hyphen itself.

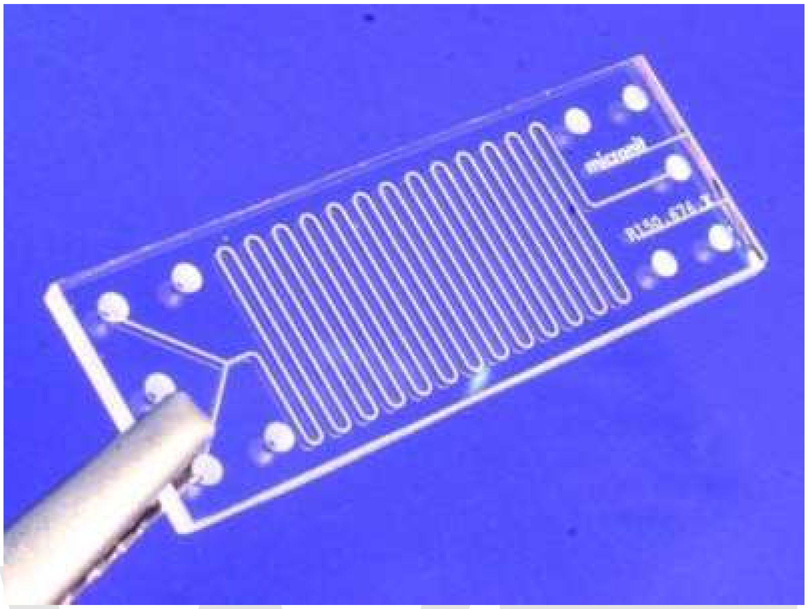
Microscopy



Fluorescence microscope image of two mouse cell nuclei in prophase (scale bar is 5 µm).

The visualization of single molecules, single cells, biological tissues and nanomaterials is an important and attractive approach in analytical science. Also, hybridization with other traditional analytical tools is revolutionizing analytical science. Microscopy can be categorized into three different fields: optical microscopy, electron microscopy, and scanning probe microscopy. Recently, this field is rapidly progressing because of the rapid development of the computer and camera industries.

Lab-on-a-chip

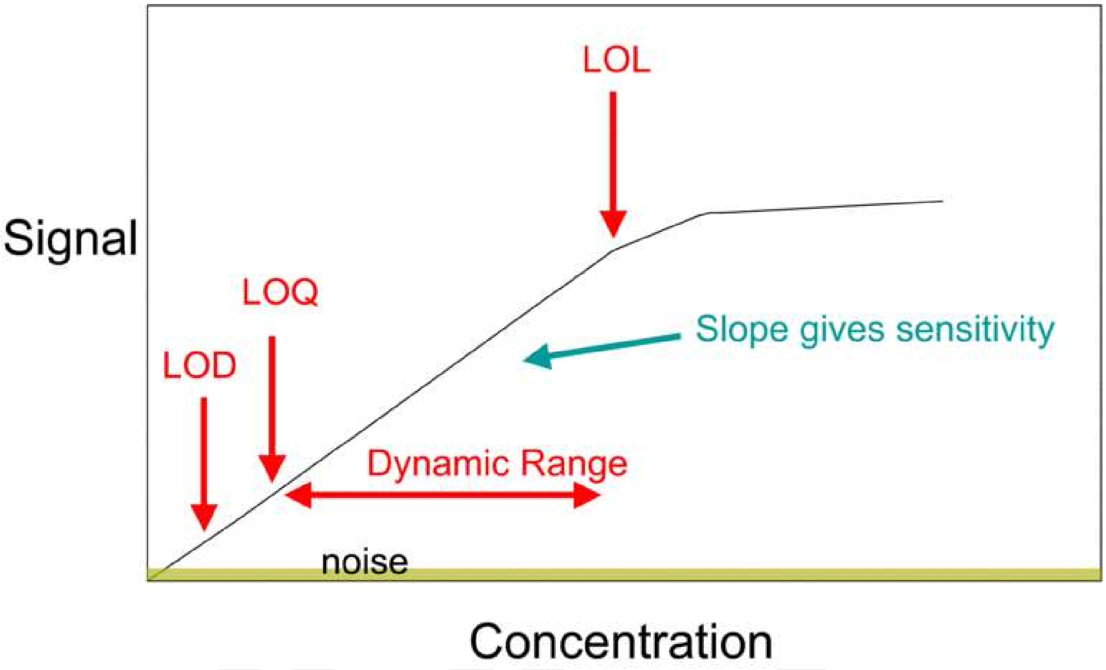


A glass microreactor

Devices that integrate (multiple) laboratory functions on a single chip of only millimeters to a few square centimeters in size and that are capable of handling extremely small fluid volumes down to less than pico liters.

Standards

Standard curve



A calibration curve plot showing limit of detection (LOD), limit of quantification (LOQ), dynamic range, and limit of linearity (LOL).

A general method for analysis of concentration involves the creation of a calibration curve. This allows for determination of the amount of a chemical in a material by comparing the results of unknown sample to those of a series known standards. If the concentration of element or compound in a sample is too high for the detection range of the technique, it can simply be diluted in a pure solvent. If the amount in the sample is below an instrument's range of measurement, the method of addition can be used. In this method a known quantity of the element or compound under study is added, and the difference between the concentration added, and the concentration observed is the amount actually in the sample.

Internal standards

Sometimes an internal standard is added at a known concentration directly to an analytical sample to aid in quantitation. The amount of analyte present is then determined relative to the internal standard as a calibrant.

Standard addition

The method of standard addition is used in instrumental analysis to determine concentration of a substance (analyte) in an unknown sample by comparison to a set of samples of known concentration, similar to using a calibration curve. Standard addition can be applied to most analytical techniques and is used instead of a calibration curve to solve the matrix effect problem.

Signals and noise

One of the most important components of analytical chemistry is maximizing the desired signal while minimizing the associated noise. The analytical figure of merit is known as the signal-to-noise ratio (S/N or SNR).

Noise can arise from environmental factors as well as from fundamental physical processes.

Thermal noise

Thermal noise results from the motion of charge carriers (usually electrons) in an electrical circuit generated by their thermal motion. Thermal noise is white noise meaning that the power spectral density is constant throughout the frequency spectrum.

The root mean square value of the thermal noise in a resistor is given by

$$v_{RMS} = \sqrt{4k_B T R \Delta f},$$

where k_B is Boltzmann's constant, T is the temperature, R is the resistance, and Δf is the bandwidth of the frequency f.

Shot noise

Shot noise is a type of electronic noise that occurs when the finite number of particles (such as electrons in an electronic circuit or photons in an optical device) is small enough to give rise to statistical fluctuations in a signal.

Shot noise is a Poisson process and the charge carriers that make up the current follow a Poisson distribution. The root mean square current fluctuation is given by

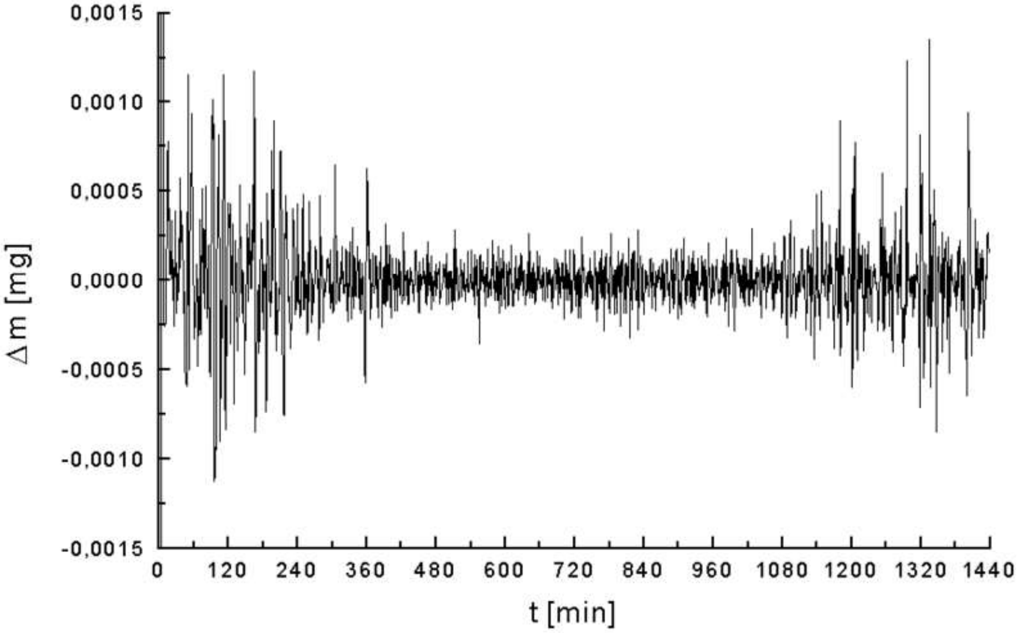
$$i_{RMS} = \sqrt{2\, e\, I\, \Delta f}$$

where e is the elementary charge and I is the average current. Shot noise is white noise.

Flicker noise

Flicker noise is electronic noise with a $1/f$ frequency spectrum; as f increases, the noise decreases. Flicker noise arises from a variety of sources, such as impurities in a conductive channel, generation and recombination noise in a transistor due to base current, and so on. This noise can be avoided by modulation of the signal at a higher frequency, for example through the use of a lock-in amplifier.

Environmental noise



Noise in a thermogravimetric analysis; lower noise in the middle of the plot results from less human activity (and environmental noise) at night.

Environmental noise arises from the surroundings of the analytical instrument. Sources of electromagnetic noise are power lines, radio and television stations, wireless devices and electric motors. Many of these noise sources are narrow bandwidth and therefore can be avoided. Temperature and vibration isolation may be required for some instruments.

Noise reduction

Noise reduction can be accomplished either in hardware or software. Examples of hardware noise reduction are the use of shielded cable, analog filtering, and signal modulation. Examples of software noise reduction are digital filtering, ensemble average, boxcar average, and correlation methods.

Applications

Analytical chemistry research is largely driven by performance (sensitivity, selectivity, robustness, linear range, accuracy, precision, and speed), and cost (purchase, operation, training, time, and space). Among the main branches of contemporary analytical atomic spectrometry, the most widespread and universal are optical and mass spectrometry. In the direct elemental analysis of solid samples, the new leaders are laser-induced breakdown and laser ablation mass spectrometry, and the related techniques with transfer of the laser ablation products into inductively coupled plasma. Advances in design of diode lasers and optical parametric oscillators promote developments in fluorescence and ionization spectrometry and also in absorption techniques where uses of optical cavities for increased effective absorption pathlength are expected to expand. Steady progress and growth in applications of plasma- and laser-based methods are noticeable. An interest towards the absolute (standardless) analysis has revived, particularly in the emission spectrometry.

A lot of effort is put in shrinking the analysis techniques to chip size. Although there are few examples of such systems competitive with traditional analysis techniques, potential advantages include size/portability, speed, and cost. (micro Total Analysis System (µTAS) or Lab-on-a-chip). Microscale chemistry reduces the amounts of chemicals used.

Much effort is also put into analyzing biological systems. Examples of rapidly expanding fields in this area are:

- Genomics - DNA sequencing and its related research. Genetic fingerprinting and DNA microarray are very popular tools and research fields.
- Proteomics - the analysis of protein concentrations and modifications, especially in response to various stressors, at various developmental stages, or in various parts of the body.
- Metabolomics - similar to proteomics, but dealing with metabolites.
- Transcriptomics - mRNA and its associated field
- Lipidomics - lipids and its associated field
- Peptidomics - peptides and its associated field
- Metalomics - similar to proteomics and metabolomics, but dealing with metal concentrations and especially with their binding to proteins and other molecules.

Analytical chemistry has played critical roles in the understanding of basic science to a variety of practical applications, such as biomedical applications, environmental monitoring, quality control of industrial manufacturing, forensic science and so on.

The recent developments of computer automation and information technologies have innervated analytical chemistry to initiate a number of new biological fields. For example, automated DNA sequencing machines were the basis to complete human genome projects leading to the birth of genomics. Protein identification and peptide sequencing by mass spectrometry opened a new field of proteomics. Furthermore, a number of ~omics based on analytical chemistry have become important areas in modern biology.

Also, analytical chemistry has been an indispensable area in the development of nanotechnology. Surface characterization instruments, electron microscopes and scanning probe microscopes enables scientists to visualize atomic structures with chemical characterizations.

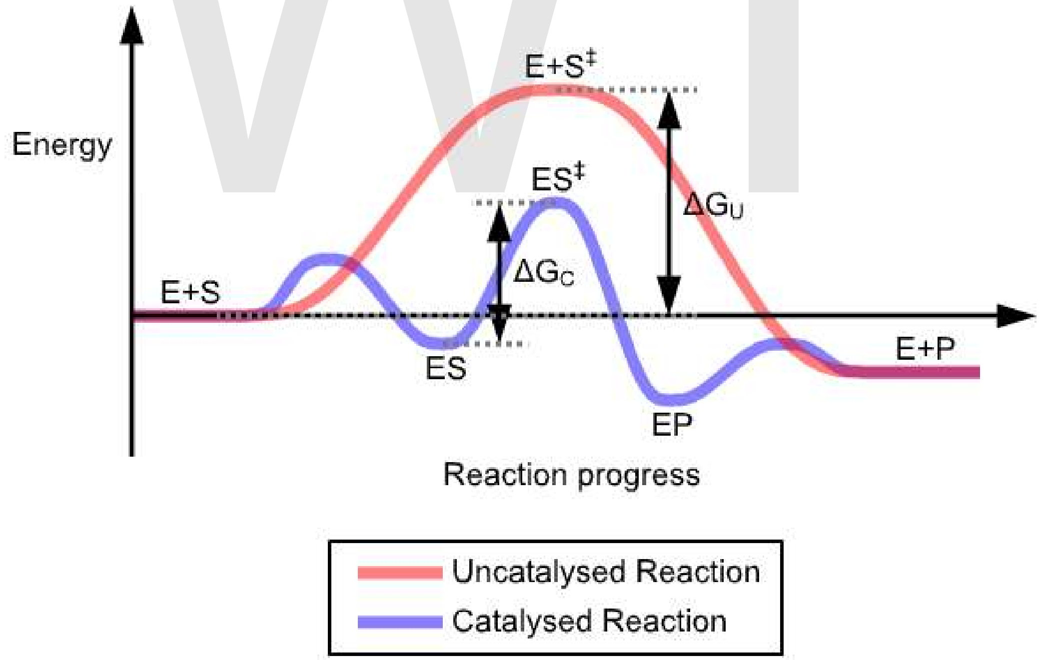
Among active contemporary analytical chemistry research fields, micro total analysis system is considered as a great promise of revolutionary technology. In this approach, integrated and miniaturized analytical systems are being developed to control and analyze single cells and single molecules. This cutting-edge technology has a promising potential of leading a new revolution in science as integrated circuits did in computer developments.

Chapter 15

Enzyme Catalysis

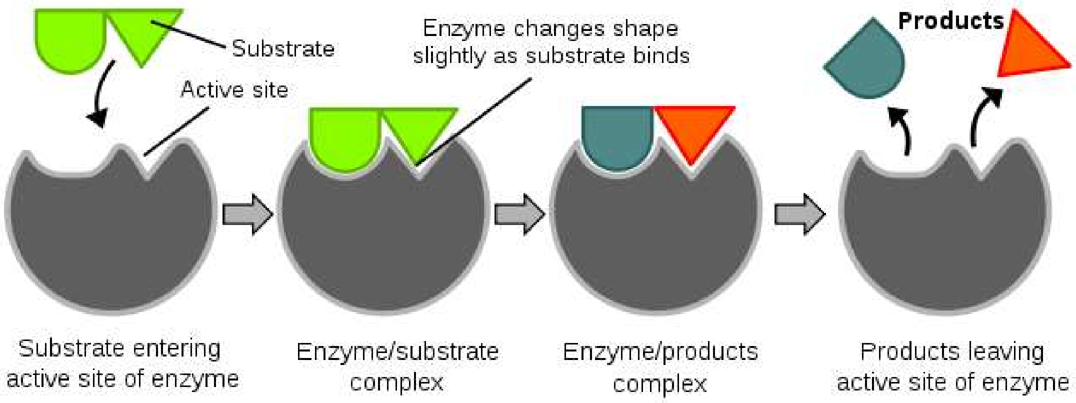
Enzyme catalysis is the catalysis of chemical reactions by specialized proteins known as enzymes. Catalysis of biochemical reactions in the cell is vital due to the very low reaction rates of the uncatalysed reactions.

The mechanism of enzyme catalysis is similar in principle to other types of chemical catalysis. By providing an alternative reaction route and by stabilizing intermediates the enzyme reduces the energy required to reach the highest energy transition state of the reaction. The reduction of activation energy (Ea) increases the number of reactant molecules with enough energy to reach the activation energy and form the product.



Stabilization of the transition state by an enzyme.

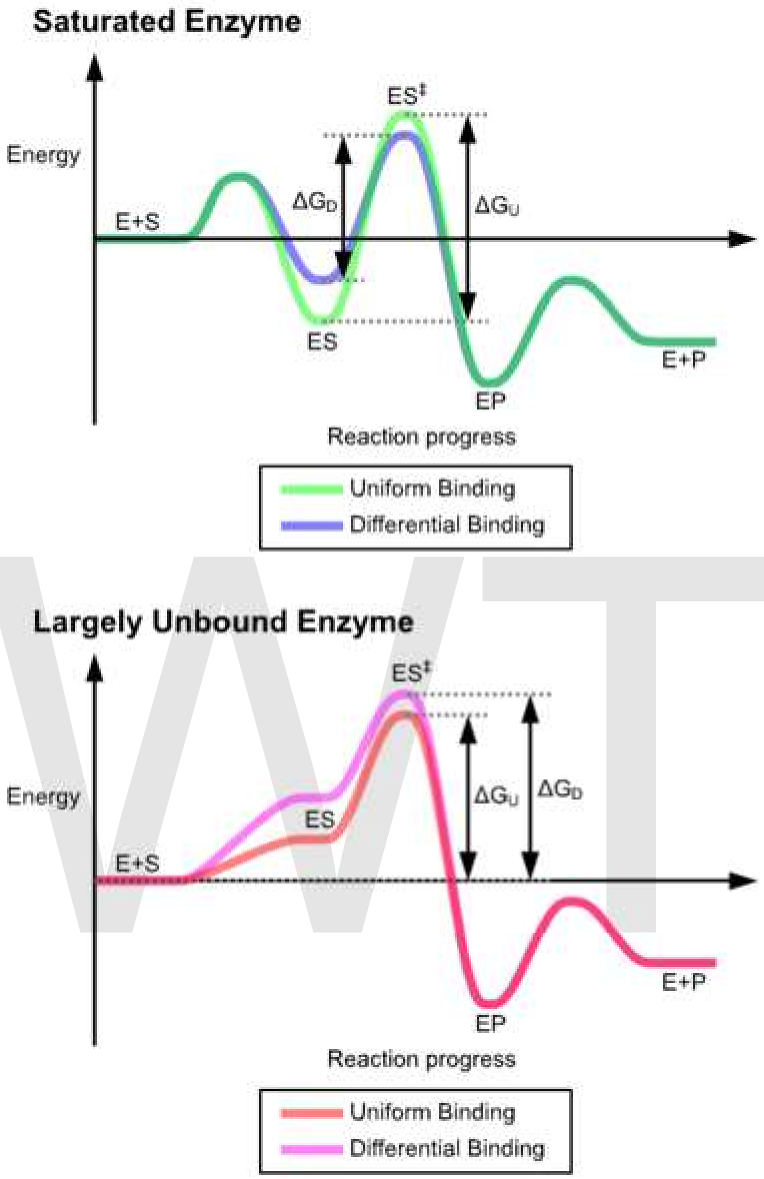
Induced fit



Diagrams to show the induced fit hypothesis of enzyme action.

The favored model for the enzyme-substrate interaction is the induced fit model. This model proposes that the initial interaction between enzyme and substrate is relatively weak, but that these weak interactions rapidly induce conformational changes in the enzyme that strengthen binding.

Catalysis by induced fit



The different mechanisms of substrate binding

The advantages of the induced fit mechanism arise due to the stabilizing effect of strong enzyme binding. There are two different mechanisms of substrate binding: uniform binding, which has strong substrate binding, and differential binding, which has strong transition state binding. The stabilizing effect of uniform binding increases both substrate and transition state binding affinity, while differential binding increases only transition state binding affinity. Both are used by enzymes and have been evolutionarily chosen to minimize the Ea of the reaction. Enzymes which are saturated, that is, have a high affinity substrate binding, require differential binding to reduce the Ea, whereas small substrate unbound enzymes may use either differential or uniform binding.

These effects have led to most proteins using the differential binding mechanism to reduce the Ea, so most proteins have high affinity of the enzyme to the transition state. Differential binding is carried out by the induced fit mechanism - the substrate first binds weakly, then the enzyme changes conformation increasing the affinity to the transition state and stabilizing it, so reducing the activation energy to reach it.

It is important to clarify, however, that the induced fit concept cannot be used to rationalize catalysis. That is, the chemical catalysis is defined as the reduction of $Ea^{\ddagger}$ (when the system is already in the $ES^{\ddagger}$) relative to $Ea^{\ddagger}$ in the uncatalyzed reaction in water (without the enzyme). The induced fit only suggests that the barrier is lower in the closed form of the enzyme but does not tell us what the reason for the barrier reduction is.

Induced fit may be beneficial to the fidelity of molecular recognition in the presence of competition and noise via the conformational proofreading mechanism .

Mechanisms of transition state stabilization

These conformational changes also bring catalytic residues in the active site close to the chemical bonds in the substrate that will be altered in the reaction. After binding takes place, one or more mechanisms of catalysis lowers the energy of the reaction's transition state, by providing an alternative chemical pathway for the reaction. There are six possible mechanisms of "over the barrier" catalysis as well as a "through the barrier" mechanism:

Catalysis by bond strain

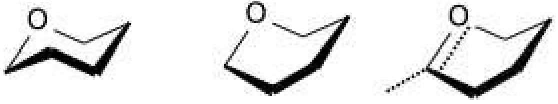
This is the principal effect of induced fit binding, where the affinity of the enzyme to the transition state is greater than to the substrate itself. This induces structural rearrangements which strain substrate bonds into a position closer to the conformation of the transition state, so lowering the energy difference between the substrate and transition state and helping catalyze the reaction.

However, the strain effect is, in fact, a ground state destabilization effect, rather than transition state stabilization effect. Furthermore, enzymes are very flexible and they cannot apply large strain effect.

In addition to bond strain in the substrate, bond strain may also be induced within the enzyme itself to activate residues in the active site.

For example:

Substrate, bound substrate, and transition state conformations of lysozyme.



The substrate, on binding, is distorted from the typical 'chair' hexose ring into the 'sofa' conformation, which is similar in shape to the transition state.

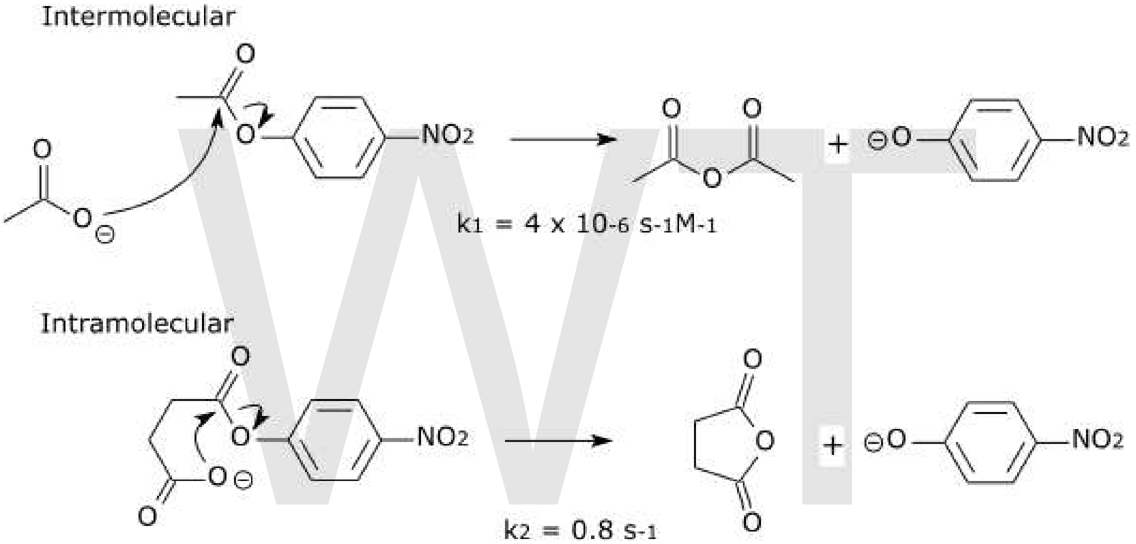
Catalysis by proximity and orientation

This increases the rate of the reaction as enzyme-substrate interactions align reactive chemical groups and hold them close together. This reduces the entropy of the reactants and thus makes reactions such as ligations or addition reactions more favorable, there is a reduction in the overall loss of entropy when two reactants become a single product.

This effect is analogous to an effective increase in concentration of the reagents. The binding of the reagents to the enzyme gives the reaction intramolecular character, which gives a massive rate increase.

For example:

Similar reactions will occur far faster if the reaction is intramolecular.



The effective concentration of acetate in the intramolecular reaction can be estimated as $k_2/k_1 = 2 \times 10^5$ *Molar.*

However, the situation might be more complex, since modern computational studies have established that traditional examples of proximity effects cannot be related directly to enzyme entropic effects. Also, the original entropic proposal has been found to largely overestimate the contribution of orientation entropy to catalysis.

Catalysis involving proton donors or acceptors (Acid/Base Catalysis)

Proton donors and acceptors, i.e. acids and bases, may donate and accept protons in order to stabilize developing charges in the transition state. This typically has the effect of activating nucleophile and electrophile groups, or stabilizing leaving groups. Histidine is often the residue involved in these acid/base reactions, since it has a pKa close to neutral pH and can therefore both accept and donate protons.

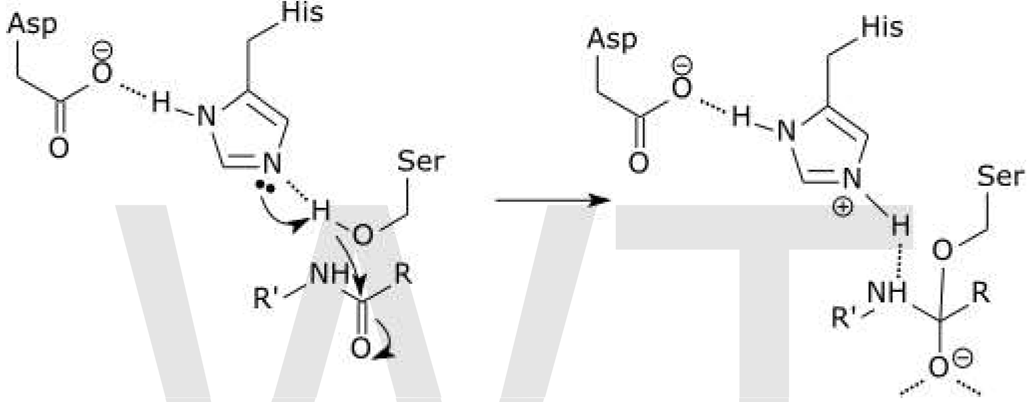
Many reaction mechanisms involving acid/base catalysis assume a substantially altered pKa. This alteration of pKa is possible through the local environment of the residue.

Conditions	Acids	Bases
Hydrophobic environment	Increase pKa	Decrease pKa
Adjacent residues of like charge	Increase pKa	Decrease pKa
Salt bridge (and hydrogen bond) formation	Decrease pKa	Increase pKa

The pKa is can be modified significantly by the environment, to the extent that residues which are basic in solution may act as proton donors, and vice versa.

For example:

Serine protease catalytic mechanism



The initial step of the serine protease catalytic mechanism involves the histidine of the active site accepting a proton from the serine residue. This prepares the serine as a nucleophile to attack the amide bond of the substrate. This mechanism includes donation of a proton from serine (a base, pKa 14) to histidine (an acid, pKa 6), made possible due to the local environment of the bases.

It is important to clarify that the modification of the pKa's is a pure part of the electrostatic mechanism. Furthermore, the catalytic effect of the above example is mainly associated with the reduction of the pKa of the oxy anion and the increase in the pKa of the histidine, while the proton transfer from the serine to the histidine is not catalyzed significantly, since it is not the rate determining barrier.

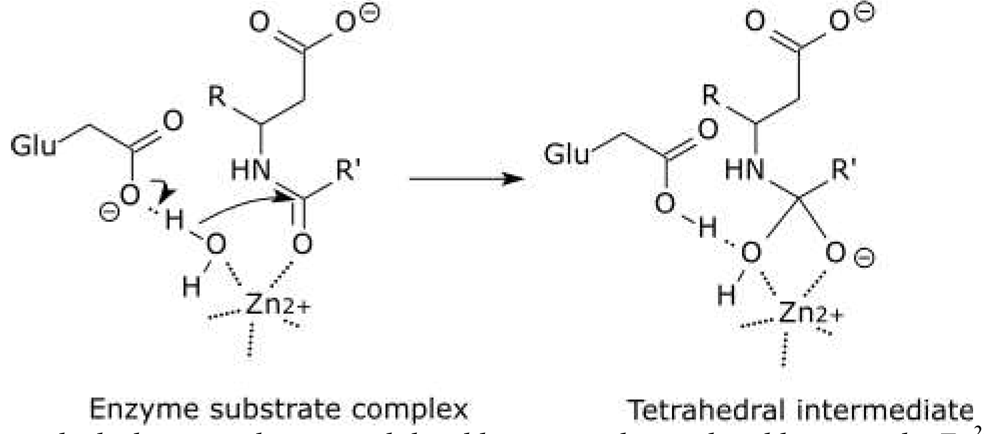
Electrostatic catalysis

Stabilization of charged transition states can also be by residues in the active site forming ionic bonds (or partial ionic charge interactions) with the intermediate. These bonds can either come from acidic or basic side chains found on amino acids such as lysine, arginine, aspartic acid or glutamic acid or come from metal cofactors such as zinc. Metal ions are particularly effective and can reduce the pKa of water enough to make it an effective nucleophile.

Systematic computer simulation studies established that electrostatic effects give, by far, the largest contribution to catalysis. In particular, it has been found that enzyme provides an environment which is more polar than water, and that the ionic transition states are stabilized by fixed dipoles. This is very different from transition state stabilization in water, where the water molecules must pay with "reorganization energy". in order to stabilize ionic and charged states. Thus, the catalysis is associated with the fact that the enzyme polar groups are preorganized

For example:

Carboxypeptidase catalytic mechanism



The tetrahedral intermediate is stabilised by a partial ionic bond between the Zn^{2+} *ion and the negative charge on the oxygen.*

Covalent catalysis

Covalent catalysis involves the substrate forming a transient covalent bond with residues in the active site or with a cofactor. This adds an additional covalent intermediate to the reaction, and helps to reduce the energy of later transition states of the reaction. The covalent bond must, at a later stage in the reaction, be broken to regenerate the enzyme. This mechanism is found in enzymes such as proteases like chymotrypsin and trypsin, where an acyl-enzyme intermediate is formed. Schiff base formation using the free amine from a lysine residue is another mechanism, as seen in the enzyme aldolase during glycolysis.

Some enzymes utilize non-amino acid cofactors such as pyridoxal phosphate (PLP) or thiamine pyrophosphate (TPP) to form covalent intermediates with reactant molecules. Such covalent intermediates function to reduce the energy of later transition states, similar to how covalent intermediates formed with active site amino acid residues allow stabilization, but the capabilities of cofactors allow enzymes to carryout reactions that amino acid side residues alone could not. Enzymes utilizing such cofactors include the PLP-dependent enzyme aspartate transaminase and the TPP-dependent enzyme pyruvate dehydrogenase.

It is important to clarify that covalent catalysis does correspond in most cases to simply the use of a specific mechanism rather than to true catalysis. For example, the energetics of the covalent bond to the serine molecule in chymotrypsin should be compared to the well-understood covalent bond to the nucleophile in the uncatalyzed solution reaction. A true proposal of a covalent catalysis (where the barrier is lower than the corresponding barrier in solution) would require, for example, a partial covalent bond to the transition state by an enzyme group (e.g., a very strong hydrogen bond), and such effects do not contribute significantly to catalysis.

Quantum tunneling

These traditional "over the barrier" mechanisms have been challenged in some cases by models and observations of "through the barrier" mechanisms (quantum tunneling). Some enzymes operate with kinetics which are faster than what would be predicted by the classical $\Delta G^{\ddagger}$. In "through the barrier" models, a proton or an electron can tunnel through activation barriers. Quantum tunneling for protons has been observed in tryptamine oxidation by aromatic amine dehydrogenase.

Interestingly, quantum tunneling does not appear to provide a major catalytic advantage, since the tunneling contributions are similar in the catalyzed and the uncatalyzed reactions in solution.. However, the tunneling contribution (typically enhancing rate constants by a factor of ~1000 compared to the rate of reaction for the classical 'over the barrier' route) is likely crucial to the viability of biological organisms. This emphasizes the general importance of tunneling reactions in biology.

In 1971-1972 the first quantum-mechanical model of enzyme catalysis was formulated.

Examples of catalytic mechanisms

In reality, most enzyme mechanisms involve a combination of several different types of catalysis.

Triose phosphate isomerase

Triose phosphate isomerase (EC 5.3.1.1) catalyses the reversible interconvertion of the two triose phosphates isomers dihydroxyacetone phosphate and D-glyceraldehyde 3-phosphate.

Trypsin

Trypsin (EC 3.4.21.4) is a serine protease that cleaves protein substrates at lysine and arginine amino acid residues.

Aldolase

Aldolase (EC 4.1.2.13) catalyses the breakdown of fructose 1,6-bisphosphate (F-1,6-BP) into glyceraldehyde 3-phosphate and dihydroxyacetone phosphate (DHAP).

Chapter 16

Mass Balance

A **mass balance** (also called a material balance) is an application of conservation of mass to the analysis of physical systems. By accounting for material entering and leaving a system, mass flows can be identified which might have been unknown, or difficult to measure without this technique. The exact conservation law used in the analysis of the system depends on the context of the problem but all revolve around mass conservation, i.e. that matter cannot disappear or be created spontaneously.

Therefore, mass balances are used widely in engineering and environmental analyses. For example mass balance theory is used to design chemical reactors, analyse alternative processes to produce chemicals as well as in pollution dispersion models and other models of physical systems. Closely related and complementary analysis techniques include the population balance, energy balance and the somewhat more complex entropy balance. These techniques are required for thorough design and analysis of systems such as the refrigeration cycle.

In environmental monitoring the term **budget calculations** is used to describe mass balance equations where they are used to evaluate the monitoring data (comparing input and output, etc.) In biology the dynamic energy budget theory for metabolic organisation makes explicit use of time, mass and energy balances.

Introduction

The general form quoted for a mass balance is *The mass that enters a system must, by conservation of mass, either leave the system or accumulate within the system* .

Mathematically the mass balance for a system without a chemical reaction is as follows:

$$\text{Input} = \text{Output} + \text{Accumulation}$$

Strictly speaking the above equation holds also for systems with chemical reactions if the terms in the balance equation are taken to refer to total mass i.e. the sum of all the chemical species of the system. In the absence of a chemical reaction the amount of any chemical species flowing in and out will be the same; This gives rise to an equation for each species in the system. However if this is not the case then the mass balance equation must be amended to allow for the generation or depletion (consumption) of each chemical species. Some use one term in this equation to account for chemical reactions, which will be negative for depletion and positive for generation. However, the conventional form of this equation is written to account for both a positive generation term (i.e. product of reaction) and a negative consumption term (the reactants used to produce the products). Although overall one term will account for the total balance on the system, if this balance equation is to be applied to an individual species and then the entire process, both terms are necessary. This modified equation can be used not only for reactive systems, but for population balances such as occur in particle mechanics problems. The amended equation is given below; Note that it simplifies to the earlier equation in the case that the generation term is zero.

$$\text{Input} + \text{Generation} = \text{Output} + \text{Accumulation} + \text{Consumption}$$

- In the absence of a nuclear reaction the number of atoms flowing in and out are the same, even in the presence of a chemical reaction
- To perform a balance the boundaries of the system must be well defined
- Mass balances can be taken over physical systems at multiple scales.
- Mass balances can be simplified with the assumption of steady state, where the accumulation term is zero

Illustrative example

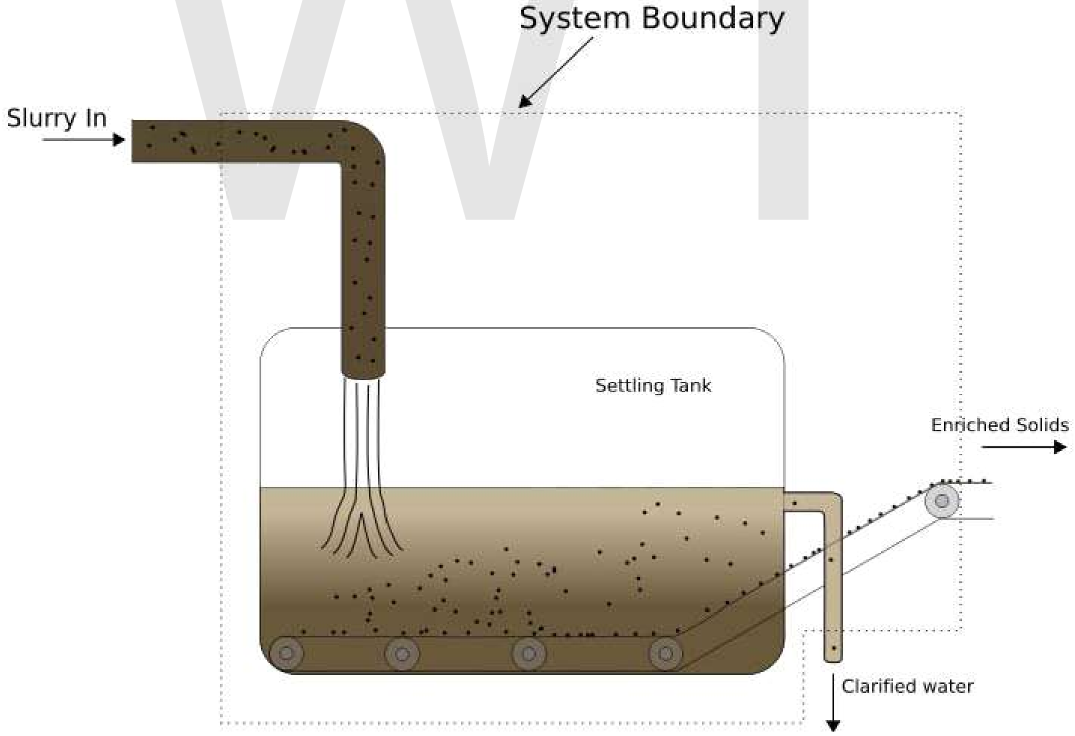


Diagram showing clarifier example

At this point a simple example shall be given for illustrative purposes. Consider the situation whereby a slurry is flowing into a settling tank to remove the solids in the tank, solids are collected at the bottom by means of a conveyor belt partially submerged in the tank, water exits via an overflow outlet.

In this example we shall consider there to be two species, solids and water. The species are concentrated in each of the output streams, that is to say that the water to solid ratio at the water overflow outlet is higher than at the slurry inlet and the solids concentration at the exit of the conveyor belt is higher than that at the slurry inlet.

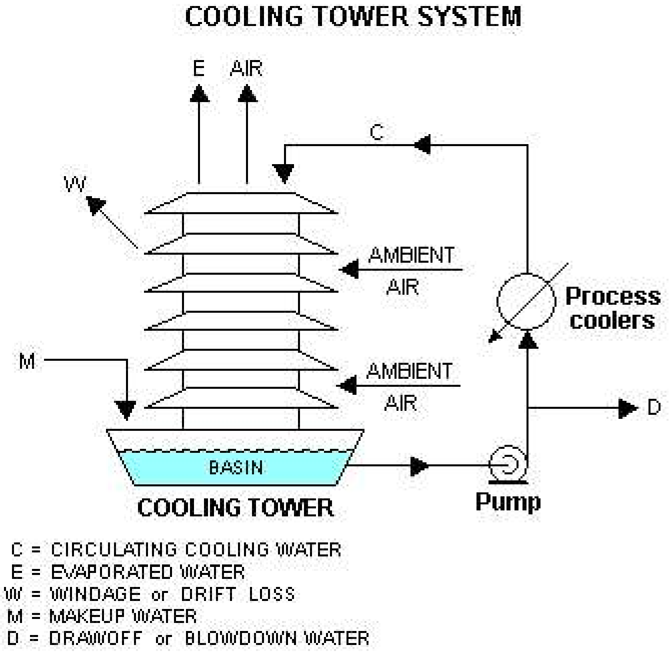
Assumptions

- Steady state
- Non-reactive system

Analysis

The slurry inlet composition has been measured by sampling the inlet and has a composition (by mass) of 50% solid and 50% water, with a mass flow of 100 kg per minute, the tank is assumed to be operating at steady state, and as such accumulation is zero, so input and output must be equal for both the solids and water. If we know that the removal efficiency for the slurry tank is 60%, then the water outlet will contain 20kg/min of solids (40% times 100kg/min times 50% solids). If we measure the flow rate of combined solids and water the water outlet to be 60kg per minute then the amount of water exiting via the conveyor belt is 10kg/min. This allows us to completely determine how the mass has been distributed in the system with only limited information and using the mass balance relations across the system boundaries

Mass feedback (recycle)



Cooling towers are a good example of a recycle system

Mass balances can be performed across systems which have cyclic flows. In these systems output streams are fed back into the input of a unit for often for further reprocessing.

Such systems are common in grinding circuits, where materials are crushed then sieved to only allow a particular size of particle out of the circuit and the larger particles are returned to the grinder. However recycle flows are by no means restricted to solid mechanics operations, they are used in liquid and gas flows as well. One such example is in cooling towers, where water is pumped through the cooling tower many times, with only a small quantity of water drawn off at each pass (to prevent solids build up) until it has either evaporated or exited with the drawn off water.

The use of the recycle aids in increasing overall conversion of input products, which is useful for low per-pass conversion processes, for example the Haber process.

Differential mass balances

A mass balance can also be taken differentially. The concept is the same as for a large mass balance, however it is performed in the context of a limiting system (for example, one can consider the limiting case in time or, more commonly, volume). The use of a differential mass balance is to generate differential equations that can be used to provide an understanding and effective modelling tool for the target system.

The differential mass balance is usually solved in two steps, firstly a set of governing differential equations must be obtained, and then these equations must be solved, either analytically or, for less tractable problems, numerically.

A good example of the applications of differential mass balance are shown in the following systems:

1. Ideal (stirred) Batch reactor
2. Ideal tank reactor, also named Continuous Stirred Tank Reactor (CSTR)
3. Ideal Plug Flow Reactor (PFR)

Ideal batch reactor

A closed system. Many chemistry textbooks implicitly assume that the studied system can be described as a batch reactor when they write about reaction kinetics and chemical equilibrium. The mass balance for a substance A becomes

IN + PROD = OUT + ACC

$$0 + r_A V = 0 + \frac{dn_A}{dt}$$

where r_A denotes the rate at which substance A is produced, V is the volume (which may be constant or not), n_A the number of moles (n) of substance A.

In a fed-batch reactor some reactants/ingredients are added continuously or in pulses (compare making porridge by either first blending all ingredients and the let it boil, which can be described as a batch reactor, or by first mixing only water and salt and making that boil before the other ingredients are added, which can be described as a fed-batch reactor). Mass balances for fed-batch reactors become a bit more complicated.

Reactive example

In this example we will use the law of mass action to **derive** the expression for a chemical equilibrium constant.

Assume we have a closed reactor in which the following liquid phase reversible reaction occurs:

$$aA + bB \leftrightarrow cC + dD$$

The mass balance for substance A becomes

IN + PROD = OUT + ACC

$$0 + r_A V = 0 + \frac{dn_A}{dt}$$

As we have a liquid phase reaction we can (usually) assume a constant volume and since $n_A = V * C_A$ we get

$$r_{\mathrm{A}}V = V\frac{dC_{\mathrm{A}}}{dt}$$

or

$$r_{\mathrm{A}} = \frac{dC_{\mathrm{A}}}{dt}$$

In many text books this is given as the definition of reaction rate without specifying the implicit assumption that we are talking about reaction rate in a closed system with only one reaction. This is an unfortunate mistake that has confused many students over the years.

According to the law of mass action the forward reaction rate can be written as

$r_1 = k_1[\mathrm{A}]^a[\mathrm{B}]^b$

and the backward reaction rate as

$r_{-1} = k_{-1}1[\mathrm{C}]^c[\mathrm{D}]^d$

The rate at which substance A is produced is thus

$r_{\mathrm{A}} = r_{-1} - r_1$

and since, at equilibrium, the concentration of A is constant we get

$$r_{\mathrm{A}} = r_{-1} - r_1 = \frac{dC_{\mathrm{A}}}{dt} = 0$$

or, rearranged

$$\frac{k_1}{k_{-1}} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = K_{eq}$$

Ideal tank reactor/continuously stirred tank reactor

An open system. A lake can be regarded as a tank reactor and lakes with long turnover times (e.g. with a low flux to volume ratio) can for many purposes be regarded as continuously stirred (e.g. homogeneous in all respects). The mass balance becomes

IN + PROD = OUT + ACC

$$Q_0 \cdot C_{\mathrm{A},0} + r_A \cdot V = Q \cdot C_{\mathrm{A}} + \frac{dn_{\mathrm{A}}}{dt}$$

where Q_0 and Q denote the volumetric flow in and out of the system respectively and $C_{\mathrm{A},0}$ and C_{A} the concentration of A in the inflow and outflow respective. In an open system we can never reach a chemical equilibrium. We can, however, reach a steady state where all **state variables** (temperature, concentrations etc.) remain constant (ACC = 0)

Example

Consider a bathtub in which we have some bathing salt dissolved. We now fill in more water, keeping the bottom plug in. What happens?

Since there is no reaction, PROD = 0 and since there is no outflow $Q = 0$. The mass balance becomes

IN + PROD = OUT + ACC

$$Q_0 \cdot C_{\mathrm{A},0} + 0 = 0 \cdot C_{\mathrm{A}} + \frac{dn_{\mathrm{A}}}{dt}$$

or

$$Q_0 \cdot C_{\mathrm{A},0} = \frac{dC_{\mathrm{A}}V}{dt} = V\frac{dC_{\mathrm{A}}}{dt} + C_{\mathrm{A}}\frac{dV}{dt}$$

Using a mass balance for total volume, however, it is evident that $\frac{dV}{dt} = Q_0$ and that $V = V_{t=0} + Q_0 t$. Thus we get

$$\frac{dC_{\mathrm{A}}}{dt} = \frac{Q_0}{(V_{t=0} + Q_0 t)}\left(C_{\mathrm{A},0} - C_{\mathrm{A}}\right)$$

Note that there is no reaction and hence no reaction rate or rate law involved, and yet $\frac{dC_{\mathrm{A}}}{dt} \neq 0$. We can thus draw the conclusion that reaction rate can not be defined in a general manner using $\frac{dC}{dt}$. One **must** first write down a mass balance before a link between $\frac{dC}{dt}$ and the reaction rate can be found. Many textbooks, however, define reaction rate as

$$v = \frac{dC_{\mathrm{A}}}{dt}$$

without mentioning that this definition implicitly assumes that the system is closed, has a constant volume and that there is only one reaction.

Ideal plug flow reactor (PFR)

An open system with no mixing along the reactor but perfect mixing across the reactor. Often used for systems like rivers and water pipes if the flow is turbulent. When a mass balance is made for a tube, one first considers an infinitesimal part of the tube and make a mass balance over that using the ideal tank reactor model. That mass balance is then integrated over the entire reactor volume to obtain:

$$\frac{d(Q \cdot C_A)}{dV} = r_A$$

In numeric solutions, e.g. when using computers, the ideal tube is often translated to a series of tank reactors, as it can be shown that a PFR is equivalent to an infinite number of stirred tanks in series, but the latter is often easier to analyze, especially at steady state.

More complex problems

In reality, reactors are often non-ideal, in which combinations of the reactor models above are used to describe the system. Not only chemical reaction rates, but also mass transfer rates may be important in the mathematical description of a system, especially in heterogeneous systems.

As the chemical reaction rate depends on temperature it is often necessary to make both an energy balance (often a heat balance rather than a full fledged energy balance) as well as mass balances to fully describe the system. A different reactor models might be needed for the energy balance: A system that is closed with respect to mass might be open with respect to energy e.g. since heat may enter the system through conduction.

Commercial use

In industrial process plants, using the fact that the mass entering and leaving any portion of a process plant must balance, data validation and reconciliation algorithms may be employed to correct measured flows, provided that enough redundancy of flow measurements exist to permit statistical reconciliation and exclusion of detectably erroneous measurements. Since all real world measured values contain inherent error, the reconciled measurements provide a better basis than the measured values do for financial reporting, optimization, and regulatory reporting. Software packages exist to make this commercially feasible on a daily basis.

Mass balance of ice sheets

The mass balance concept can usefully be applied to ice sheets, which is of interest because of their relevance to sea level rise.

For example, the average precipitation over the Antarctic ice sheet is approximately 150 mm / year; the average ice depth is 3 km; therefore the average residence time of the ice within the ice sheet is approximately 20,000 years.