Essentials of
Chemical Engineering

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Chemical Engineering

Process engineers design, construct and operate plants

Chemical engineering is the branch of engineering that deals with the application of physical science (e.g., chemistry and physics), and life sciences (e.g., biology, microbiology and biochemistry) with mathematics and economics, to the process of converting raw materials or chemicals into more useful or valuable forms. In addition to producing useful materials, modern chemical engineering is also concerned with pioneering valuable new materials and techniques - such as nanotechnology, fuel cells and biomedical engineering. Chemical engineering largely involves the design, improvement and maintenance of processes involving chemical or biological transformations for large-scale manufacture. Chemical engineers ensure the processes are operated safely, sustainably and economically. Chemical engineers in this branch are usually employed under the title of **process engineer**. A related term with a wider definition is chemical technology. A person employed in this field is called a chemical engineer.

Chemical engineering timeline

In 1824, French physicist Sadi Carnot, in his "On the Motive Power of Fire", was the first to study the thermodynamics of combustion reactions. In the 1850s, German physicist Rudolf Clausius began to apply the principles developed by Carnot to chemical systems at the atomic to molecular scale. During the years 1873 to 1876 at Yale University, American mathematical physicist Josiah Willard Gibbs, the first to be awarded a Ph.D. in engineering in the U.S., in a series of three papers, developed a mathematical-based, graphical methodology, for the study of chemical systems using the thermodynamics of Clausius. In 1882, German physicist Hermann von Helmholtz, published a founding thermodynamics paper, similar to Gibbs, but with more of an electro-chemical basis, in which he showed that measure of chemical affinity, i.e., the "force" of chemical reactions, is determined by the measure of the free energy of the reaction process. The following timeline shows some of the key steps in the development of the science of chemical engineering:

- **1805** – John Dalton published Atomic Weights, allowing chemical equations to be balanced and the basis for chemical engineering mass balances.
- **1882** – a course in "Chemical Technology" is offered at University College London
- **1883** – Osborne Reynolds defines the dimensionless group for fluid flow, leading to practical scale-up and understanding of flow, heat and mass transfer
- **1885** – Henry Edward Armstrong offers a course in "chemical engineering" at Central College (later Imperial College), London.
- **1888** – There is a Department of Chemical Engineering at Glasgow and West of Scotland Technical College offering day and evening classes.
- **1888** – Lewis M. Norton starts a new curriculum at Massachusetts Institute of Technology (MIT): Course X, Chemical Engineering
- **1889** – Rose Polytechnic Institute awards the first bachelor's of science in chemical engineering in the US.
- **1891** – MIT awards a bachelor's of science in chemical engineering to William Page Bryant and six other candidates.
- **1892** – A bachelor's program in chemical engineering is established at the University of Pennsylvania.
- **1898** – Bachelor of science program in chemical engineering is established at the University of Michigan.

- **1901** – George E. Davis produces the *Handbook of Chemical Engineering*
- **1905** – the University of Wisconsin awards the first Ph.D. in chemical engineering to Oliver Patterson Watts.
- **1908** – the American Institute of Chemical Engineers (AIChE) is founded.
- **1922** – the UK Institution of Chemical Engineers (IChemE) is founded.

Applications

Chemical engineering is applied in the manufacture of a wide variety of products. The chemical industry has a large scope, manufacturing inorganic and organic industrial chemicals, ceramics, fuels and petrochemicals, agrochemicals (fertilizers, insecticides, herbicides), plastics and elastomers, oleochemicals, explosives, detergents and detergent products (soap, shampoo, cleaning fluids), fragrances and flavors, additives, dietary supplements and pharmaceuticals. Closely allied or overlapping disciplines include wood processing, food processing, environmental technology, and the engineering of petroleum, glass, paints and other coatings, inks, sealants and adhesives. A variety of substances found in everyday life have been made under the supervision of a chemical engineer.

Overview

Chemical engineers operate processes at plants, above is the image of processes at an industry control room

Chemical engineers design processes to ensure the most economical operation. This means that the entire production chain must be planned and controlled for costs. A chemical engineer can both simplify and complicate "showcase" reactions for an economic advantage. Using a higher pressure or temperature makes several reactions easier; ammonia, for example, is simply produced from its component elements in a high-pressure reactor. On the other hand, reactions with a low yield can be recycled continuously, which would be complex, arduous work if done by hand in the laboratory. It is not unusual to build 6-step, or even 12-step evaporators to reuse the vaporization energy for an economic advantage. In contrast, laboratory chemists evaporate samples in a single step.

The individual processes used by chemical engineers (e.g., distillation or filtration) are called unit operations and consist of chemical reactions, mass-, heat- and momentum-transfer operations. Unit operations are grouped together in various configurations for the purpose of chemical synthesis and/or chemical separation. Some processes are a combination of intertwined transport and separation unit operations, (e.g., reactive distillation).

Three primary physical laws underlying chemical engineering design are conservation of mass, conservation of momentum and conservation of energy. The movement of mass and energy around a chemical process are evaluated using mass balances and energy balances, laws that apply to discrete parts of equipment, unit operations, or an entire plant. In doing so, chemical engineers must also use principles of thermodynamics, reaction kinetics, fluid mechanics and transport phenomena. The task of performing these balances is now aided by process simulators, which are complex software models that can solve mass and energy balances and usually have built-in modules to simulate a variety of common unit operations.

Design

Chemical engineers design chemical production equipment and entire chemical plants:

- Piping and pump sizing and specification
- Chemical reactors
    - Continuous stirred-tank reactor
    - Plug flow reactor
    - Catalytic reactor
- Separation equipment
    - Distillation column
    - Extraction column
    - Evaporation
    - Filtering
    - Reverse osmosis
- Process Systems Engineering
    - Process control and instrumentation

Design is worked through in a number of phases. With the process concept and intended chemical reactions in hand, a flowsheet is designed, which includes all material flows in the process, including not only starting materials and products, but all intermediates, wastes and unit operations. Preliminary design is done to approximate cost, space and environmental requirements to further evaluate the viability of the concept. Later stages require the design and specification of all parts and each piece of equipment in the process, and finally, cost calculation and project planning. Supervision of the work, testing, simulation follow. Running the process and its maintenance continues, with continual improvement, for the life of the process, followed by shutdown and cleanup of the site.

Modern chemical engineering

The modern discipline of chemical engineering encompasses much more than just process engineering. Chemical engineers are now engaged in the development and production of a diverse range of products, as well as in commodity and specialty chemicals. These products include high performance materials needed for aerospace, automotive, biomedical, electronic, environmental, space and military applications. Examples include ultra-strong fibers, fabrics, dye-sensitized solar cells, adhesives and composites for vehicles, bio-compatible materials for implants and prosthetics, gels for medical applications, pharmaceuticals, and films with special dielectric, optical or spectroscopic properties for opto-electronic devices. Additionally, chemical engineering is often intertwined with biology and biomedical engineering. Many chemical engineers work on biological projects such as understanding biopolymers (proteins) and mapping the human genome. The line between chemists and chemical engineers is growing ever more thin as more and more chemical engineers begin to start their own innovation using their knowledge of chemistry, physics and mathematics to create, implement and mass produce their ideas.

Related fields and topics

Today, the field of chemical engineering is a diverse one, covering areas from biotechnology and nanotechnology to mineral processing.

- Biochemical engineering
- Bioinformatics
- Biomedical engineering
- Biomolecular engineering
- Biotechnology
- Ceramics
- Chemical process modeling
- Chemical
- Heat transfer
- Industrial gas
- Mass transfer
- Materials science
- Metallurgy
- Microfluidics
- Mineral processing
- Nanotechnology
- Natural environment
- Natural gas
- Process design
- Process development
- Process Systems Engineering
- Process miniaturization
- Paper engineering
- Safety engineering
- Semiconductor device fabrication
- Separation processes
    - Crystallization processes

Technologist

- Chemical reactor
- Computational fluid dynamics
- Corrosion engineering
- Electrochemistry
- Environmental engineering
- Earthquake engineering
- Fluid dynamics
- Food engineering
- Fuel cell

processing

- Nuclear reprocessing
- Oil exploration
- Oil refinery
- Pharmaceutical engineering
- Plastics engineering
- Polymers
- Process control

    - Distillation processes
    - Membrane processes
- Textile engineering
- Thermodynamics
- Transport phenomena
- Unit operations
- Water technology

Additional topics under the title *AIChE's Technical Divisions and Forums* in American Institute of Chemical Engineers

Chapter- 2

Chemical Reactor

In chemical engineering, **chemical reactors** are vessels designed to contain chemical reactions. The design of a chemical reactor deals with multiple aspects of chemical engineering. Chemical engineers design reactors to maximize net present value for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product while requiring the least amount of money to purchase and operate. Normal operating expenses include energy input, energy removal, raw material costs, labor, etc. Energy changes can come in the form of heating or cooling, pumping to increase pressure, frictional pressure loss (such as pressure drop across a 90^o elbow or an orifice plate), agitation, etc.

Chemical reaction engineering is the branch of chemical engineering which deals with chemical reactors and their design, especially by application of chemical kinetics.

Overview

Cut-away view of a stirred-tank chemical reactor with a cooling jacket

Chemical reactor with half coils wrapped around it

There are a couple main basic vessel types:

- A tank
- A pipe or tubular reactor

Both types can be used as continuous reactors or batch reactors. Most commonly, reactors are run at steady-state, but can also be operated in a transient state. When a reactor is first brought back into operation (after maintenance or inoperation) it would be considered to be in a transient state, where key process variables change with time. Both types of reactors may also accommodate one or more solids (reagents, catalyst, or inert materials), but the reagents and products are typically liquids and gases.

There are three main basic models used to estimate the most important process variables of different chemical reactors:

- *batch reactor* model (batch),
- *continuous stirred-tank reactor* model (CSTR), and
- *plug flow reactor* model (PFR).

Furthermore, catalytic reactors require separate treatment, whether they are batch, CST, or PF reactors, as the many assumptions of the simpler models are not valid.

Key process variables include

- Residence time (τ, lower case Greek tau)
- Volume (V)
- Temperature (T)
- Pressure (P)
- Concentrations of chemical species (C_1, C_2, C_3, ... C_n)
- Heat transfer coefficients (h, U)

A chemical reactor, typically tubular reactor, could be a packed bed. The packing inside the bed may have catalyst to catalyze the chemical reaction. A chemical reactor may also be a fluidized bed.

Chemical reactions occurring in a reactor may be exothermic, meaning giving off heat, or endothermic, meaning absorbing heat. A chemical reactor vessel may have a cooling or heating jacket or cooling or heating coils (tubes) wrapped around the outside of its vessel wall to cool down or heat up the contents.

Types

CSTR (Continuous Stirred-Tank Reactor)

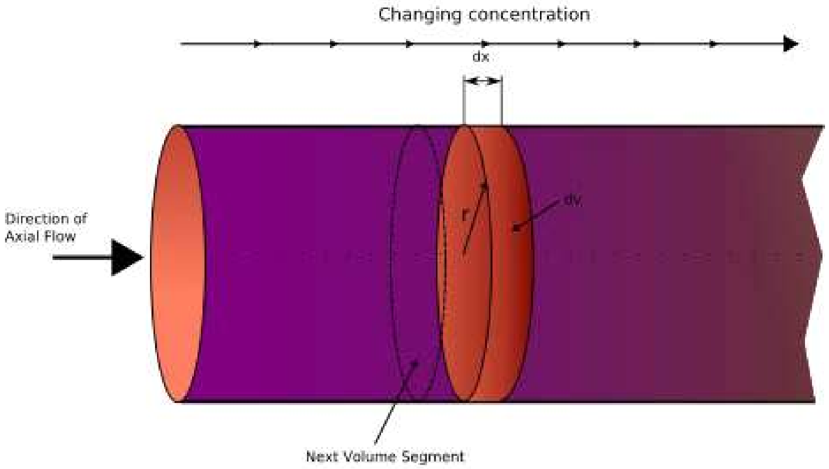
Reactor CSTR. Check of a condition of the case. Note the impeller (or agitator) blades on the shaft for mixing. Also note the baffle at the bottom of the image which also helps in mixing.

In a CSTR, one or more fluid reagents are introduced into a tank reactor equipped with an impeller while the reactor effluent is removed. The impeller stirs the reagents to ensure proper mixing. Simply dividing the volume of the tank by the average volumetric flow rate through the tank gives the *residence time*, or the average amount of time a discrete quantity of reagent spends inside the tank. Using chemical kinetics, the reaction's expected percent completion can be calculated. Some important aspects of the CSTR:

- At steady-state, the flow rate in must equal the mass flow rate out, otherwise the tank will overflow or go empty (transient state). While the reactor is in a transient state the model equation must be derived from the differential mass and energy balances.
- The reaction proceeds at the reaction rate associated with the final (output) concentration.
- Often, it is economically beneficial to operate several CSTRs in series. This allows, for example, the first CSTR to operate at a higher reagent concentration and therefore a higher reaction rate. In these cases, the sizes of the reactors may be varied in order to minimize the total capital investment required to implement the process.
- It can be seen that an infinite number of infinitely small CSTRs operating in series would be equivalent to a PFR.

The behavior of a CSTR is often approximated or modeled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR). All calculations performed with CISTRs assume perfect mixing. If the residence time is 5-10 times the mixing time, this approximation is valid for engineering purposes. The CISTR model is often used to simplify engineering calculations and can be used to describe research reactors. In practice it can only be approached, in particular in industrial size reactors.

PFR (Plug Flow Reactor)



Simple diagram illustrating plug flow reactor model

In a PFR, one or more fluid reagents are pumped through a pipe or tube. The chemical reaction proceeds as the reagents travel through the PFR. In this type of reactor, the changing reaction rate creates a gradient with respect to distance traversed; at the inlet to the PFR the rate is very high, but as the concentrations of the reagents decrease and the concentration of the product(s) increases the reaction rate slows. Some important aspects of the PFR:

- All calculations performed with PFRs assume no upstream or downstream mixing, as implied by the term "plug flow".
- Reagents may be introduced into the PFR at locations in the reactor other than the inlet. In this way, a higher efficiency may be obtained, or the size and cost of the PFR may be reduced.
- A PFR typically has a higher efficiency than a CSTR of the same volume. That is, given the same space-time, a reaction will proceed to a higher percentage completion in a PFR than in a CSTR.

For most chemical reactions, it is impossible for the reaction to proceed to 100% completion. The rate of reaction decreases as the percent completion increases until the point where the system reaches dynamic equilibrium (no net reaction, or change in chemical species occurs). The equilibrium point for most systems is less than 100% complete. For this reason a separation process, such as distillation, often follows a chemical reactor in order to separate any remaining reagents or byproducts from the desired product. These reagents may sometimes be reused at the beginning of the process, such as in the Haber process.

Continuous oscillatory baffled reactor (COBR) is a tubular plug flow reactor. The mixing in COBR is achieved by the combination of fluid oscillation and orifice baffles, allowing plug flow to be achieved under laminar flow conditions with the net flow Reynolds number just about 100.

Semi-batch reactor

A semi-batch reactor is operated with both continuous and batch inputs and outputs. A fermenter, for example, is loaded with a batch, which constantly produces carbon dioxide, which has to be removed continuously. Analogously, driving a reaction of gas with a liquid is usually difficult, since the gas bubbles off. Therefore, a continuous feed of gas is injected into the batch of a liquid. An example of such a reaction is chlorination.

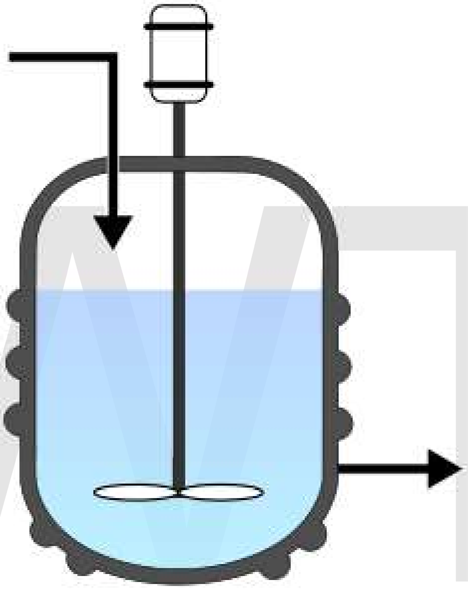
Catalytic reactor

Although catalytic reactors are often implemented as plug flow reactors, their analysis requires more complicated treatment. The rate of a catalytic reaction is proportional to the amount of catalyst the reagents contact. With a solid phase catalyst and fluid phase reagents, this is proportional to the exposed area, efficiency of diffusion of reagents in and products out, and turbulent mixing or lack thereof. Perfect mixing cannot be assumed. Furthermore, a catalytic reaction pathway is often multi-step with intermediates that are chemically bound to the catalyst; and as the chemical binding to the catalyst is also a chemical reaction, it may affect the kinetics.

The behavior of the catalyst is also a consideration. Particularly in high-temperature petrochemical processes, catalysts are deactivated by sintering, coking, and similar processes.

A common example of a catalytic reactor is the catalytic converter following an engine.

Continuous stirred-tank reactor



CSTR symbol

The **continuous stirred-tank reactor** (**CSTR**), also known as vat- or backmix reactor, is a common ideal reactor type in chemical engineering. A CSTR often refers to a model used to estimate the key unit operation variables when using a continuous agitated-tank reactor to reach a specified output. The mathematical model works for all fluids: liquids, gases, and slurries.

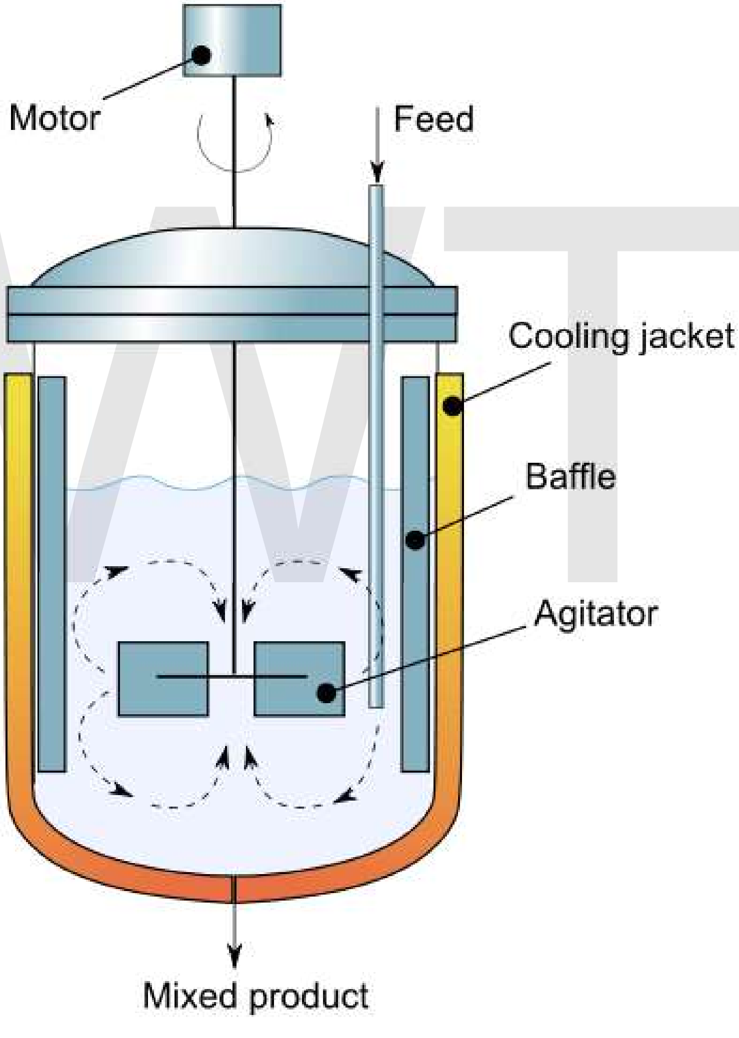
The behavior of a CSTR is often approximated or modeled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR). All calculations performed with CISTRs assume perfect mixing. In a perfectly mixed reactor, the output composition is identical to composition of the material inside the reactor, which is a function of residence time and rate of reaction. If the residence time is 5-10 times the mixing time, this approximation is valid for engineering purposes. The CISTR model is often used to simplify engineering calculations and can be used to describe research reactors. In practice it can only be approached, in particular in industrial size reactors.

Assume:

- perfect or ideal mixing, as stated above

Integral mass balance on number of moles N_i of species i in a reactor of volume V.
[*accumulation*] = [*in*] − [*out*] + [*generation*]

1. $$\frac{dN_i}{dt} = F_{io} - F_i + V\nu_i r_i$$



Cross-sectional diagram of **Continuous stirred-tank reactor**

where F_{io} is the molar flow rate inlet of species i, F_i the molar flow rate outlet, and ν_i stoichiometric coefficient. The reaction rate, r, is generally dependent on the reactant concentration and the rate constant (k). The rate constant can be determined by using a known empirical reaction rates that is adjusted for temperature using the Arrhenius temperature dependence. Generally, as the temperature increases so does the rate at which the reaction occurs. Residence time, τ, is the average amount of time a discrete quantity of reagent spends inside the tank.

Assume:

- constant density (valid for most liquids; valid for gases only if there is no net change in the number of moles or drastic temperature change)
- isothermal conditions, or constant temperature (k is constant)
- steady state
- single, irreversible reaction ($\nu_A = -1$)
- first-order reaction ($r = kC_A$)

A → products

$N_A = C_A V$ (where C_A is the concentration of species A, V is the volume of the reactor, N_A is the number of moles of species A)

2. $$C_A = \frac{C_{Ao}}{1 + k\tau}$$

The values of the variables, outlet concentration and residence time, in Equation 2 are major design criteria.

To model systems that do not obey the assumptions of constant temperature and a single reaction, additional dependent variables must be considered. If the system is considered to be in unsteady-state, a differential equation or a system of coupled differential equations must be solved.

CSTR's are known to be one of the systems which exhibit complex behavior such as steady-state multiplicity, limit cycles and chaos.

Chapter- 3

Paper Engineering

Paper Science & Engineering (also called **Bioprocess Engineering**, **Chemical Engineering** and/or **Biochemical Engineering**) is a branch of engineering that deals with the usage of physical science (e.g. chemistry and physics) and life sciences (e.g. biology and biochemistry) in conjunction with mathematics as applied to the converting of renewable raw materials into useful and valuable products. The field applies various principles in process engineering and unit operations to the manufacture of paper, chemicals, energy and related materials. The following timeline shows some of the key steps in the development of the science of chemical and bioprocess engineering:

From a heritage perspective, the field encompasses the design and analysis of a wide variety of thermal, chemical and biochemical unit operations employed in the manufacture of pulp and paper, and addresses the preparation of its raw materials from trees or other natural resources via a pulping process, chemical and mechanical pretreatment of these recovered biopolymer (e.g. principally, although not solely, cellulose-based) fibers in a fluid suspension, the high-speed forming and initial dewatering of a non-woven web, the development of bulk sheet properties via control of energy and mass transfer operations, as well as post-treatment of the sheet with coating, calendering, and other chemical and mechanical processes.

Applications

Today, the field of Paper & Chemical Engineering is applied to the manufacture of a wide variety of products. The (bio)chemical industry scope manufactures organic and agrochemicals (fertilizers, insecticides, herbicides), oleochemicals, fragrances and flavors, food, feed, pharmaceuticals, nutraceuticals, chemicals, polymers and power from biological materials.

The resulting products of paper engineering including paper, cardboard, and various paper derivatives are widely used in everyday life. In addition to being a subset of Chemical Engineering, the field of paper engineering is closely linked to forest management, product recycling, and the mass production of paper - based media.

Methods

Mechanical Pulping

In the process of mechanical pulping, “grinding” and “refining” are the two main methods used to create the pulp. “Grinding” refers to the method of pressing logs and chips against a turning stone to produce fibers. “Refiner pulping” is the term used to describe the treatment of wood – chips with chemicals or heat, then crushing the objects between two disks, one or both of which are rotating. There are four main types of “Refiner pulping”, which include Refiner Mechanical Pulping, Thermo – mechanical Pulping, Chemi – mechanical Pulping, and Chemi – thermomechanical pulping. Further descriptions of each process are contained in this link: Mechanical pulping, when compared to chemical pulping, is relatively inexpensive and has a high pulp yield (85-95%). However, the paper created is generally weak since it retains the lignin.

Chemical Pulping

The process of chemical pulping is used to chemically disband the lignin found in the cell walls of the material undergoing the process. After the cellulose fibers are separated from the lignin, a pulp is created which can then be treated to create durable paper, boxes, and corrugated cardboard. Chemical pulping can be characterized by two main methods: sulfate (Kraft) pulping and sulfite pulping, and these two methods have different benefits. Sulfate pulping can be performed on a wide range of tree varieties and results in the creation of a strong type of paper. Conversely, sulfite pulping results in a higher volume of pulp which is easier to bleach and process. However, sulfate pulping is more widely used since the product is more durable and the chemicals used in the process can be recovered, thus resulting in minimal environmental pollution.

Further Pulp Processing

The pulp is then processed through an apparatus which renders the pulp as a mesh of fibers. This fiber network is then pressed to remove all water contents, and the paper is subsequently dried to remove all traces of moisture.

Finishing

After the above processes have been completed, the resulting paper is coated with a miniscule amount of china clay or calcium carbonate to modify the surface, and the paper is then re – sized depending on its intended purpose.

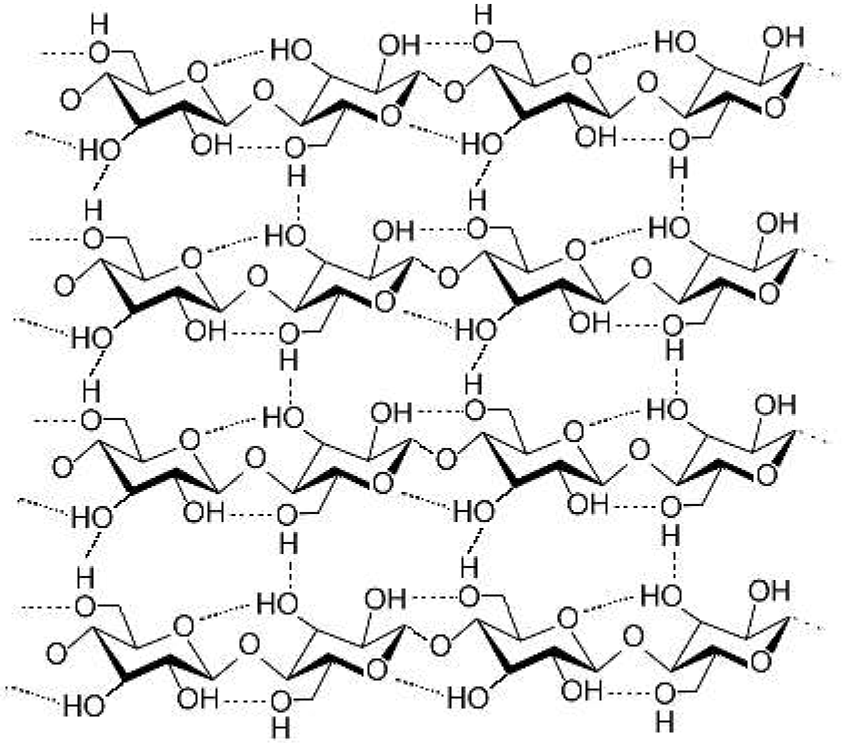
Product Recycling

Generally, the material to be recycled first undergoes mechanical or chemical pulping to render it in pulp form. The resulting pulp is then processed in the same way normal pulp is processed; however, original fiber is sometimes added to enhance the quality and appearance of the product.

Related fields and topics

Today, the field of paper & bioprocess engineering is a diverse one, covering areas from biotechnology and nanotechnology to electricity generation.

Paper engineers design, construct and operate plants



Cellulose is a natural biopolymer

- Agricultural engineering
- Biomolecular engineering
- Biochemical engineering
- Biological engineering
- Chemical process modeling
- Chemical engineering
- Chemical reactor
- Computational fluid dynamics
- Corrosion engineering
- Environmental engineering
- Fluid dynamics
- Food engineering
- Forest engineering
- Heat transfer
- Mass transfer
- Materials science
- Microfluidics
- Nanotechnology
- Natural environment
- Polymers
- Process control
- Process design
- Process development

- Safety engineering
- Separation processes
- Textile engineering
- Thermodynamics
- Transport Phenomena
- Unit operations
- Water technology

Chapter- 4

Chemical Process

In a "scientific" sense, a **chemical process** is a method or means of somehow changing one or more chemicals or chemical compounds. Such a chemical process can occur by itself or be caused by somebody. Such a chemical process commonly involves a chemical reaction of some sort. In an "engineering" sense, a **chemical process** is a method intended to be used in manufacturing or on an industrial scale to change the composition of chemical(s) or material(s), usually using technology similar or related to that used in chemical plants or the chemical industry.

Neither of these definitions is exact in the sense that one can always tell definitively what is a chemical process and what is not; they are practical definitions. There is also significant overlap in these two definition variations. Because of the inexactness of the definition, chemists and other scientists use the term "chemical process" only in a general sense or in the engineering sense. However, in the "process (engineering)" sense, the term "chemical process" is used extensively.

Although this type of chemical process may sometimes involve only one step, often multiple steps, referred to as unit operations, are involved. In a plant, each of the unit operations commonly occur in individual vessels or sections of the plant called **units**. Often, one or more chemical reactions are involved, but other ways of changing chemical (or material) composition may be used, such as mixing or separation processes. The process steps may be sequential in time or sequential in space along a stream of flowing or moving material. For a given amount of a feed (input) material or product (output) material, an expected amount of material can be determined at key steps in the process from empirical data and material balance calculations. These amounts can be scaled up or down to suit the desired capacity or operation of a particular chemical plant built for such a process. More than one chemical plant may use the same chemical process, each plant perhaps at differently scaled capacities.

Such chemical processes can be illustrated generally as **block flow diagrams** or in more detail as **process flow diagrams**. Block flow diagrams show the units as blocks and the streams flowing between them as connecting lines with arrowheads to show direction of flow.

In addition to chemical plants for producing chemicals, chemical processes with similar technology and equipment are also used in oil refining and other refineries, natural gas processing, polymer and pharmaceutical manufacturing, food processing, and water and wastewater treatment.

Unit processing in chemical engineering

Unit processing is the basic processing in chemical engineering. Together with unit operations it forms the main principle of the varied chemical industries. Each genre of unit processing follows the same chemical law much as each genre of unit operations follows the same physical law.

Chemical engineering unit processing consists of the following important processes:

- Oxidation
- Reduction
- Hydrogenation
- Dehydrogenation
- Hydrolysis
- Hydration reaction
- Dehydration
- Halogenation
- Nitrification
- Sulfonation
- Ammoniation
- Alkaline fusion
- Alkylation
- Dealkylation
- Esterification
- Polymerization
- Polycondensation
- Catalysis

Redox

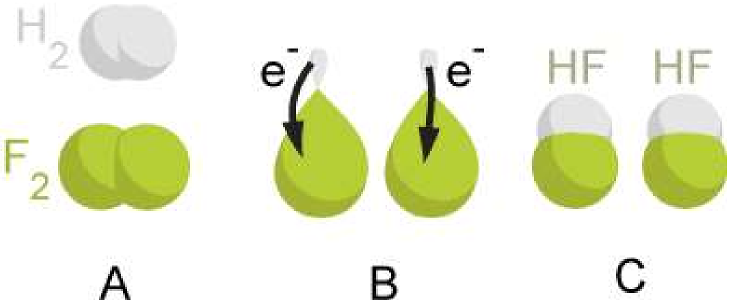


Illustration of a redox reaction

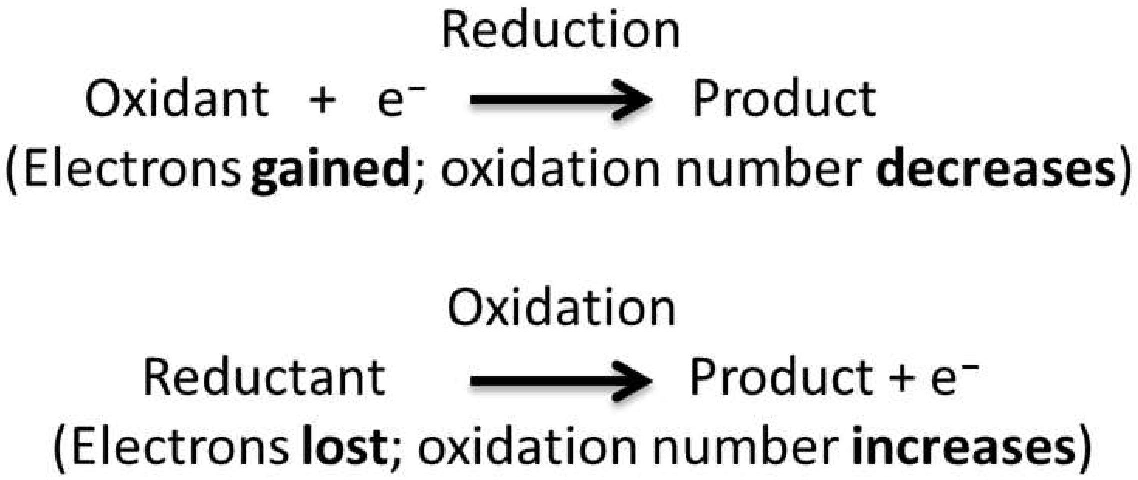
Redox (shorthand for **oxidation-reduction**) reactions describe all chemical reactions in which atoms have their oxidation number (oxidation state) changed. This can be either a simple redox process, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen to yield methane (CH_4), or a complex process such as the oxidation of sugar ($C_6H_{12}O_6$) in the human body through a series of complex electron transfer processes.

The term comes from the two concepts of **red**uction and **ox**idation. It can be explained in simple terms:

- **Oxidation** is the *loss* of electrons or an *increase* in oxidation state by a molecule, atom, or ion.
- **Reduction** is the *gain* of electrons or a *decrease* in oxidation state by a molecule, atom, or ion.

Though sufficient for many purposes, these descriptions are not precisely correct. Oxidation and reduction properly refer to *a change in oxidation number* — the actual transfer of electrons may never occur. Thus, oxidation is better defined as an *increase in oxidation number*, and reduction as a *decrease in oxidation number*. In practice, the transfer of electrons will always cause a change in oxidation number, but there are many reactions that are classed as "redox" even though no electron transfer occurs (such as those involving covalent bonds).

Non-redox reactions, which do not involve changes in formal charge, are known as metathesis reactions.



The two parts of a redox reaction

Rusting iron

A bonfire. Combustion consists of redox reactions involving free radicals.

Oxidizing and reducing agents

In redox processes the reductant transfers electrons to the oxidant. Thus, in the reaction, the reductant or *reducing agent* loses electrons and is oxidized, and the oxidant or *oxidizing agent* gains electrons and is reduced. The pair of an oxidizing and reducing agent that are involved in a particular reaction is called a **redox pair**.

Oxidizers

Substances that have the ability to **oxidize** other substances are said to be **oxidative** or **oxidizing** and are known as oxidizing agents, **oxidants**, or **oxidizers**. Put another way, the oxidant removes electrons from another substance, and is thus itself reduced. And, because it "accepts" electrons, it is also called an electron acceptor.

Oxidants are usually chemical elements or substances with elements in high oxidation numbers (e.g., H_2O_2, $MnO{-}4$, CrO_3, $Cr_2O2{-}7$, OsO_4) or highly electronegative substances/elements that can gain one or two extra electrons by oxidizing an element or substance (O, F, Cl, Br).

Reducers

Substances that have the ability to **reduce** other substances are said to be **reductive** or **reducing** and are known as reducing agents, **reductants**, or **reducers**. That is, the reductant transfers electrons to another substance, and is thus itself oxidized. And, because it "donates" electrons, it is also called an electron donor. Electron donors can also form charge transfer complexes with electron acceptors.

Reductants in chemistry are very diverse. Electropositive elemental metals, such as lithium, sodium, magnesium, iron, zinc, aluminium, carbon, are good reducing agents. These metals donate or *give away* electrons readily. *Hydride transfer reagents*, such as $NaBH_4$ and $LiAlH_4$, are widely used in organic chemistry, primarily in the reduction of carbonyl compounds to alcohols. Another method of reduction involves the use of hydrogen gas (H_2) with a palladium, platinum, or nickel catalyst. These *catalytic reductions* are used primarily in the reduction of carbon-carbon double or triple bonds.

Examples of redox reactions

A good example is the reaction between hydrogen and fluorine in which hydrogen is being oxidized and fluorine is being reduced:

$$H_2 + F_2 \rightarrow 2\ HF$$

We can write this overall reaction as two half-reactions:

the oxidation reaction:

$$H_2 \rightarrow 2\ H^+ + 2\ e-$$

and the reduction reaction:

$$F_2 + 2\ e- \longrightarrow 2\ F^-$$

Analyzing each half-reaction in isolation can often make the overall chemical process clearer. Because there is no net change in charge during a redox reaction, the number of electrons in excess in the oxidation reaction must equal the number consumed by the reduction reaction (as shown above).

Elements, even in molecular form, always have an oxidation number of zero. In the first half-reaction, hydrogen is oxidized from an oxidation number of zero to an oxidation number of +1. In the second half-reaction, fluorine is reduced from an oxidation number of zero to an oxidation number of −1.

When adding the reactions together the electrons cancel:

$H_2 \rightarrow 2\,H^+ + 2\,e^-$

$F_2 + 2\,e^- \rightarrow 2\,F^-$

$H_2 + F_2 \rightarrow 2\,H^+ + 2\,F^-$

And the ions combine to form hydrogen fluoride:

$H_2 + F_2 \rightarrow 2\,H^+ + 2\,F^- \rightarrow 2\,HF$

Displacement reactions

Redox occurs in single displacement reactions or substitution reactions. The redox component of these types of reactions is the change of oxidation state (charge) on certain atoms, not the actual exchange of atoms in the compounds.

For example, in the reaction between iron and copper (II) sulfate solution:

$Fe + CuSO_4 \rightarrow FeSO_4 + Cu$

The ionic equation for this reaction is:

$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

As two half-equations, it is seen that the iron is oxidized:

$Fe \rightarrow Fe^{2+} + 2\,e^-$

And the copper is reduced:

$Cu^{2+} + 2\,e^- \rightarrow Cu$

Other examples

- The oxidation of iron(II) to iron(III) by hydrogen peroxide in the presence of an acid:

  $Fe^{2+} \rightarrow Fe^{3+} + e^-$
  $H_2O_2 + 2\,e^- \rightarrow 2\,OH^-$
  Overall equation:
  $2\,Fe^{2+} + H_2O_2 + 2\,H^+ \rightarrow 2\,Fe^{3+} + 2\,H_2O$

- The reduction of nitrate to nitrogen in the presence of an acid (denitrification):

$2\ NO_3^- + 10\ e^- + 12\ H^+ \rightarrow N_2 + 6\ H_2O$

Iron rusting in pyrite cubes

- Oxidation of elemental iron to iron(III) oxide by oxygen (commonly known as rusting, which is similar to tarnishing):

  $4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$

- The combustion of hydrocarbons, such as in an internal combustion engine, which produces water, carbon dioxide, some partially oxidized forms such as carbon monoxide, and heat energy. Complete oxidation of materials containing carbon produces carbon dioxide.

- In organic chemistry, the stepwise oxidation of a hydrocarbon by oxygen produces water and, successively, an alcohol, an aldehyde or a ketone, a carboxylic acid, and then a peroxide.

Redox reactions in industry

The primary process of reducing ore to produce metals is discussed in Smelting.

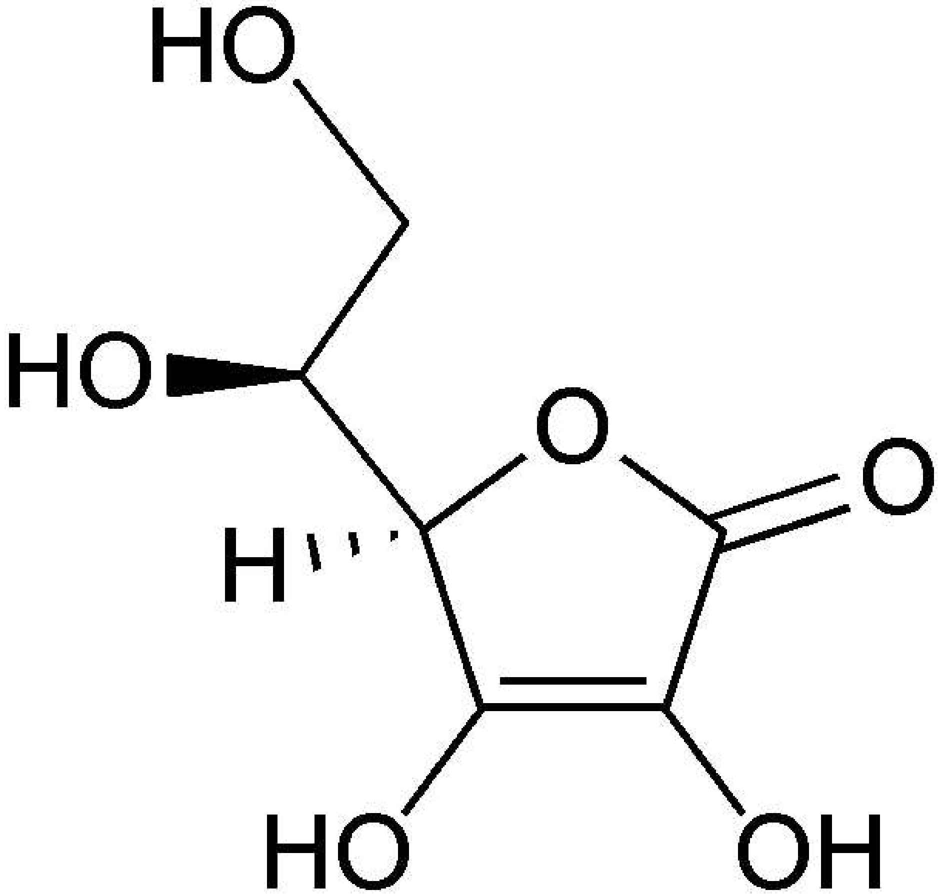
Oxidation is used in a wide variety of industries such as in the production of cleaning products and oxidizing ammonia to produce nitric acid, which is used in most fertilizers.

Redox reactions are the foundation of electrochemical cells.

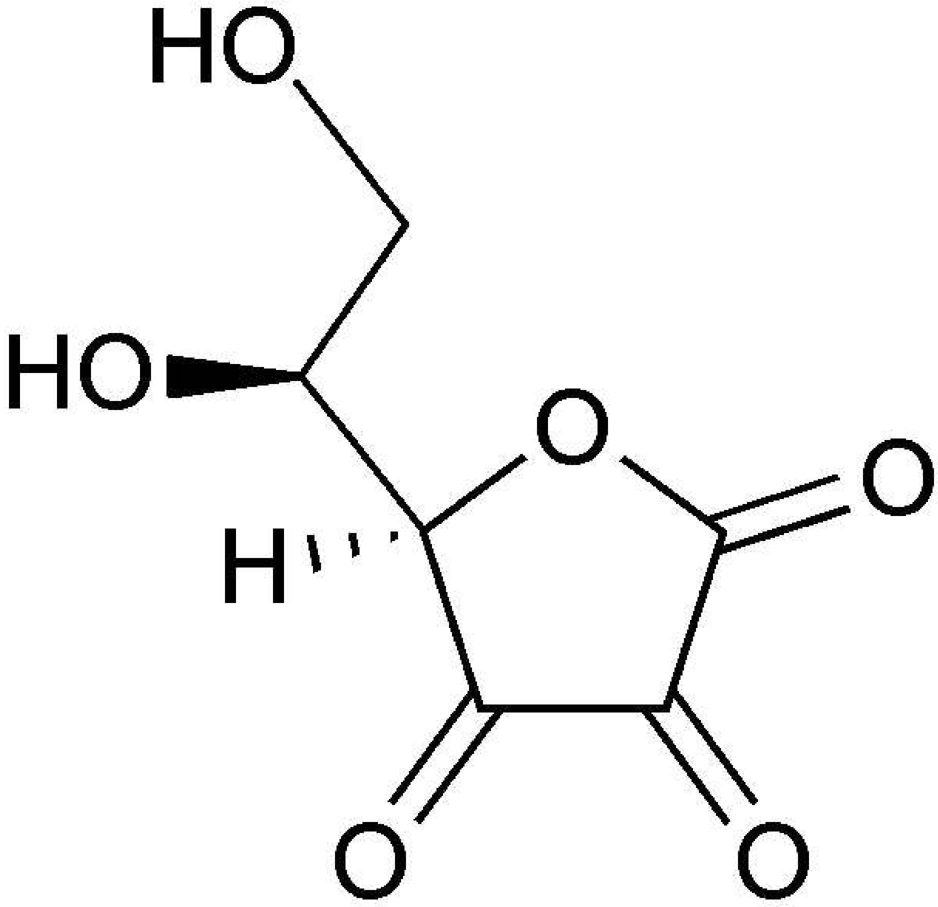
The process of electroplating uses redox reactions to coat objects with a thin layer of a material, as in chrome plated automotive parts, silver plating cutlery, and gold-plated jewelry.

The production of compact discs depends on a redox reaction, which coats the disc with a thin layer of metal film.

Redox reactions in biology



ascorbic acid (reduced form of Vitamin C)



dehydroascorbic acid (oxidized form of Vitamin C)

Many important biological processes involve redox reactions.

Cellular respiration, for instance, is the oxidation of glucose ($C_6H_{12}O_6$) to CO_2 and the reduction of oxygen to water. The summary equation for cell respiration is:

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O$$

The process of cell respiration also depends heavily on the reduction of NAD^+ to NADH and the reverse reaction (the oxidation of NADH to NAD^+). Photosynthesis and Cellular respiration are complementary but photosynthesis is not the reverse of the redox reaction in cell respiration:

$$6\ CO_2 + 6\ H_2O + \text{light energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

Biological energy is frequently stored and released by means of redox reactions. Photosynthesis involves the reduction of carbon dioxide into sugars and the oxidation of water into molecular oxygen. The reverse reaction, respiration, oxidizes sugars to produce carbon dioxide and water. As intermediate steps, the reduced carbon compounds are used to reduce nicotinamide adenine dinucleotide (NAD^+), which then contributes to the creation of a proton gradient, which drives the synthesis of adenosine triphosphate (ATP) and is maintained by the reduction of oxygen. In animal cells, mitochondria perform similar functions.

The term **redox state** is often used to describe the balance of NAD^+/NADH and $NADP^+$/NADPH in a biological system such as a cell or organ. The redox state is reflected in the balance of several sets of metabolites (e.g., lactate and pyruvate, beta-hydroxybutyrate and acetoacetate), whose interconversion is dependent on these ratios. An abnormal redox state can develop in a variety of deleterious situations, such as hypoxia, shock, and sepsis. Redox signaling involves the control of cellular processes by redox processes.

Redox proteins and their genes must be co-located for redox regulation according to the CoRR hypothesis for the function of DNA in mitochondria and chloroplasts.

Redox cycling

A wide variety of aromatic compounds are enzymatically reduced to form free radicals that contain one more electron than their parent compounds. In general, the electron donor is any of a wide variety of flavoenzymes and their coenzymes. Once formed, these anion free radicals reduce molecular oxygen to superoxide, and regenerate the unchanged parent compound. The net reaction is the oxidation of the flavoenzyme's coenzymes and the reduction of molecular oxygen to form superoxide. This catalytic behavior has been described as futile cycle or redox cycling.

Examples of redox cycling-inducing molecules are the herbicide paraquat and other viologens and quinones such as menadione.

Redox reactions in geology

A uranium mine, near Moab, Utah. Note alternating red and white/green sandstone. This corresponds to oxidized and reduced conditions in groundwater redox chemistry. The rock forms in oxidizing conditions, and is then "bleached" to the white/green state when a reducing fluid passes through the rock. The reduced fluid can also carry uranium-bearing minerals.

In geology, redox is important to both the formation of minerals, mobilization of minerals, and in some depositional environments. In general, the redox state of most rocks can be seen in the color of the rock. Red is associated with oxidizing conditions of formation, and green is typically associated with reducing conditions. White (bleached rock) can also be associated with reducing conditions. Famous examples of redox conditions affecting geological processes include uranium deposits and Moqui marbles.

Balancing redox reactions

Describing the overall electrochemical reaction for a redox process requires a *balancing* of the component half-reactions for oxidation and reduction. For reactions in aqueous solution, this generally involves adding H^+, OH^-, H_2O, and electrons to compensate for the oxidation changes.

Acidic media

In acidic media, H^+ ions and water are added to half reactions to balance the overall reaction.

For example, when manganese(II) reacts with sodium bismuthate:

Unbalanced reaction: $Mn^{2+}(aq) + NaBiO_3(s) \rightarrow Bi^{3+}(aq) + MnO_4^-\ (aq)$

Oxidation: $4\ H_2O(l) + Mn^{2+}(aq) \rightarrow MnO{-}4(aq) + 8\ H^+(aq) + 5\ e{-}$

Reduction: $2\ e{-}+ 6\ H^+ + BiO{-}3(s) \rightarrow Bi^{3+}(aq) + 3\ H_2O(l)$

The reaction is balanced by scaling the two half-cell reactions to involve the same number of electrons (multiplying the oxidation reaction by the number of electrons in the reduction step and vice versa):

$8\ H_2O(l) + 2\ Mn^{2+}(aq) \rightarrow 2\ MnO{-}4(aq) + 16\ H^+(aq) + 10\ e{-}$

$10\ e{-}+ 30\ H^+ + 5\ BiO{-}3(s) \rightarrow 5\ Bi^{3+}(aq) + 15\ H_2O(l)$

Adding these two reactions eliminates the electrons terms and yields the balanced reaction:

$14\ H^+(aq) + 2\ Mn^{2+}(aq) + 5\ NaBiO_3(s) \rightarrow 7\ H_2O(l) + 2\ MnO{-}4(aq) + 5\ Bi^{3+}(aq) + 5\ Na^+(aq)$

Basic media

In basic media, OH^- ions and water are added to half reactions to balance the overall reaction.

For example, in the reaction between potassium permanganate and sodium sulfite:

Unbalanced reaction: $KMnO_4 + Na_2SO_3 + H_2O \rightarrow MnO_2 + Na_2SO_4 + KOH$

Reduction: $3\ e{-}+ 2\ H_2O + MnO_4^- \rightarrow MnO_2 + 4\ OH^-$

Oxidation: $2\ OH^- + SO_3^{2-} \rightarrow SO_4^{2-} + H_2O + 2\ e{-}$

Balancing the number of electrons in the two half-cell reactions gives:

$6\ e{-}+ 4\ H_2O + 2\ MnO_4^- \rightarrow 2\ MnO_2 + 8\ OH^-$

$6\ OH^- + 3\ SO_3^{2-} \rightarrow 3\ SO_4^{2-} + 3\ H_2O + 6\ e{-}$

Adding these two half-cell reactions together gives the balanced equation:

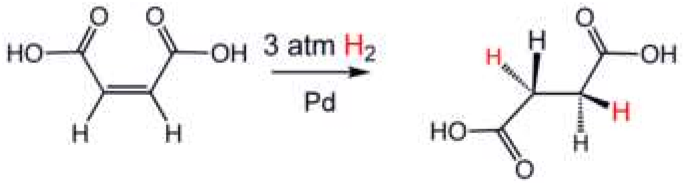
$$2\ KMnO_4 + 3\ Na_2SO_3 + H_2O \rightarrow 2\ MnO_2 + 3\ Na_2SO_4 + 2\ KOH$$

Hydrogenation

Hydrogenation, to treat with hydrogen, also a form of chemical reduction, is a chemical reaction between molecular hydrogen (H_2) and another compound or element, usually in the presence of a catalyst. The process is commonly employed to reduce or saturate organic compounds. Hydrogenation typically constitutes the addition of pairs of hydrogen atoms to a molecule, generally an alkene. Catalysts are required for the reaction to be usable; non-catalytic hydrogenation takes place only at very high temperatures. Hydrogen adds to double and triple bonds in hydrocarbons.

Because of the importance of hydrogen, many related reactions have been developed for its use. Most hydrogenations use gaseous hydrogen (H_2), but some involve the alternative sources of hydrogen, not H_2: these processes are called transfer hydrogenations. The reverse reaction, removal of hydrogen from a molecule, is called dehydrogenation. A reaction where bonds are broken while hydrogen is added is called hydrogenolysis, a reaction that may occur to carbon-carbon and carbon-heteroatom (O, N, X) bonds. Hydrogenation differs from protonation or hydride addition: in hydrogenation, the products have the same charge as the reactants.

An illustrative example of a hydrogenation reaction is the addition of hydrogen to maleic acid to succinic acid. Numerous important applications are found in the petrochemical, pharmaceutical and food industries. Hydrogenation of unsaturated fats produces saturated fats and, in some cases, trans fats.



Process

Hydrogenation has three components, the unsaturated substrate, the hydrogen (or hydrogen source) and, invariably, a catalyst. The reaction is carried out at different temperatures and pressures depending upon the substrate and the activity of the catalyst.

Substrate

The addition of H_2 to an alk*e*ne affords an alk*a*ne in the protypical reaction:

$$RCH{=}CH_2 + H_2 \rightarrow RCH_2CH_3\ (R = \text{alkyl, aryl})$$

Hydrogenation is sensitive to steric hindrance explaining the selectivity for reaction with the exocyclic double bond but not the internal double bond.

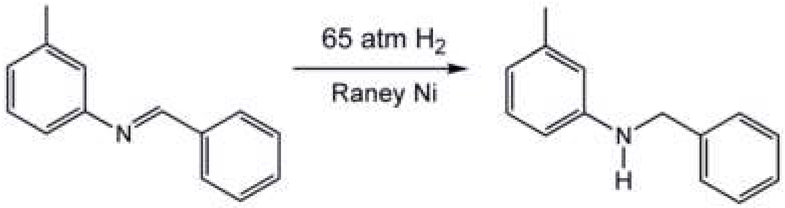
An important characteristic of alkene and alkyne hydrogenations, both the homogeneously and heterogeneously catalyzed versions, is that hydrogen addition occurs with "syn addition", with hydrogen entering from the least hindered side. Typical substrates are listed in the table

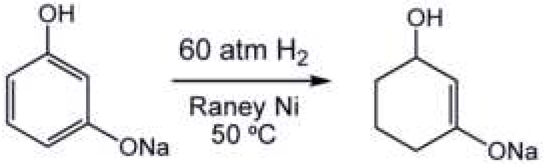
Substrates for and products of hydrogenation

alkene, $R_2C=CR'_2$	alkane, $R_2CHCHR'_2$	
alkyne, RCCR	alkene, cis-RHC=CHR'	
aldehyde, RCHO	primary alcohol, RCH_2OH	
ketone, R_2CO	secondary alcohol, R_2CHOH	
ester, RCO_2R'	two alcohols, RCH_2OH, R'OH	
imine, RR'CNR"	amine, RR'CHNHR"	
amide, $RC(O)NR'_2$	amine, $RCH_2NR'_2$	
nitrile, RCN	imine, RHCNH	easily hydrogenated further
nitro, RNO_2	amine, RNH_2	

Catalysts

With rare exception, no reaction below 480 °F occurs between H_2 and organic compounds in the absence of metal catalysts. The catalyst binds *both* the H_2 and the unsaturated substrate and facilitates their union. Platinum group metals, particularly platinum, palladium, rhodium, and ruthenium, form highly active catalysts, which operate at lower temperatures and lower pressures of H_2. Non-precious metal catalysts, especially those based on nickel (such as Raney nickel and Urushibara nickel) have also been developed as economical alternatives, but they are often slower or require higher temperatures. The trade-off is activity (speed of reaction) vs. cost of the catalyst and cost of the apparatus required for use of high pressures. Notice that the Raney-nickel catalysed hydrogenations require high pressures:

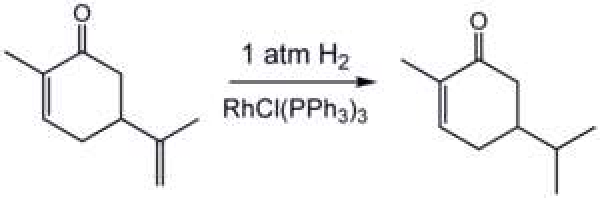




Two broad families of catalysts are known - homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts dissolve in the solvent that contains the unsaturated substrate. Heterogeneous catalysts are solids that are suspended in the same solvent with the substrate or are treated with gaseous substrate.

Homogeneous catalysts

Illustrative homogeneous catalysts include the rhodium-based compound known as Wilkinson's catalyst and the iridium-based Crabtree's catalyst. An example is the hydrogenation of carvone:



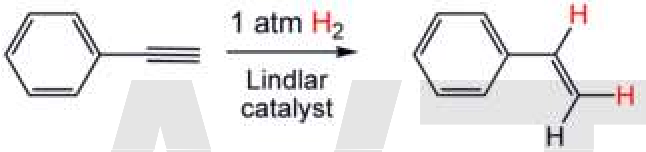
Hydrogenation is sensitive to steric hindrance explaining the selectivity for reaction with the exocyclic double bond but not the internal double bond.

The activity and selectivity of homogeneous catalysts is adjusted by changing the ligands. For prochiral substrates, the selectivity of the catalyst can be adjusted such that one enantiomeric product is favored. Asymmetric hydrogenation is also possible via heterogeneous catalysis on a metal that is modified by a chiral ligand.

Homogeneous catalysts are less active than heterogeneous catalysts.

Heterogeneous catalysts

Heterogeneous catalysts for hydrogenation are more common industrially. As in homogeneous catalysts, the activity is adjusted through changes in the environment around the metal, i.e. the coordination sphere. Different faces of a crystalline heterogeneous catalyst display distinct activities, for example. Similarly, heterogeneous catalysts are affected by their supports, i.e. the material upon with the heterogeneous catalyst is bound. In many cases, highly empirical modifications involve selective "poisons". Thus, a carefully chosen catalyst can be used to hydrogenate some functional groups without affecting others, such as the hydrogenation of alkenes without touching aromatic rings, or the selective hydrogenation of alkynes to alkenes using Lindlar's catalyst. For example, when the catalyst palladium is placed on barium sulfate and then treated with quinoline, the resulting catalyst reduces alkynes only as far as alkenes. The Lindlar catalyst has been applied to the conversion of phenylacetylene to styrene.



Asymmetric hydrogenation is also possible via heterogeneous catalysis on a metal that is modified by a chiral ligand.

Hydrogen sources

For hydrogenation, the obvious source of hydrogen is H_2 gas itself, which is typically available commercially within the storage medium of a pressurized cylinder. The hydrogenation process often uses greater than 1 atmosphere of H_2, usually conveyed from the cylinders and sometimes augmented by "booster pumps". Gaseous hydrogen is produced industrially from hydrocarbons by the process known as steam reforming.

Hydrogen may, in specialised applications, also be extracted ("transferred") from "hydrogen-donors" in place of H_2 gas. Hydrogen donors, which often serve as solvents include hydrazine, dihydronaphthalene, dihydroanthracene, isopropanol, and formic acid. In organic synthesis, transfer hydrogenation is useful for the reduction of polar unsaturated substrates, such as ketones, aldehydes, and imines.

Thermodynamics and mechanism

Hydrogenation is a strongly exothermic reaction. In the hydrogenation of vegetable oils and fatty acids, for example, the heat released is about 25 kcal per mole (105 kJ/mol), sufficient to raise the temperature of the oil by 1.6-1.7 °C per iodine number drop. The mechanism of metal-catalyzed hydrogenation of alkenes and alkynes has been extensively studied. First of all isotope labeling using deuterium confirms the regiochemistry of the addition:

$RCH{=}CH_2 + D_2 \rightarrow RCHDCH_2D$

Heterogeneous catalysis

On solids, the accepted mechanism today is called the Horiuti-Polanyi mechanism.

1. Binding of the unsaturated bond, and hydrogen dissociation into atomic hydrogen onto the catalyst
2. Addition of one atom of hydrogen; this step is reversible
3. Addition of the second atom; effectively irreversible under hydrogenating conditions.

Homogeneous catalysis

In many homogeneous hydrogenation processes, the metal binds to both components to give an intermediate alkene-metal$(H)_2$ complex. The general sequence of reactions is assumed to be as follows or a related sequence of steps:

- binding of the hydrogen to give a dihydride complex ("oxidative addition"):

  $L_nM + H_2 \rightarrow L_nMH_2$

- binding of alkene:

  $L_nM(\eta^2H_2) + CH_2{=}CHR \rightarrow L_{n-1}MH_2(CH_2{=}CHR) + L$

- transfer of one hydrogen atom from the metal to carbon (migratory insertion)

  $L_{n-1}MH_2(CH_2{=}CHR) \rightarrow L_{n-1}M(H)(CH_2\text{-}CH_2R)$

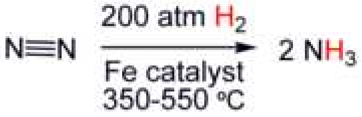
- transfer of the second hydrogen atom from the metal to the alkyl group with simultaneous dissociation of the alkane ("reductive elimination")

  $L_{n-1}M(H)(CH_2\text{-}CH_2R) \rightarrow L_{n-1}M + CH_3\text{-}CH_2R$

Preceding the oxidative addition of H_2 is the formation of a dihydrogen complex.

Inorganic substrates

The hydrogenation of nitrogen to give ammonia is conducted on a vast scale by the Haber-Bosch process, consuming an estimated 1% of the world's energy supply.



Oxygen can be partially hydrogenated to give hydrogen peroxide, although this process has not been commercialized.

Industrial applications

Catalytic hydrogenation has diverse industrial uses.

In petrochemical processes, hydrogenation is used to convert alkenes and aromatics into saturated alkanes (paraffins) and cycloalkanes (napthenes). Hydrocracking of heavy residues into diesel is another application. In isomerization and catalytic reforming processes, some hydrogen pressure is maintained to hydrogenolyze coke and prevent its accumulation.

Xylitol, a polyol, is produced by hydrogenation of the sugar xylose, an aldehyde.

In the food industry

Hydrogenation is widely applied to the processing of vegetable oils and fats. Complete hydrogenation converts unsaturated fatty acids to saturated ones. In practice the process is not usually carried to completion. Since the original oils usually contain more than one carbon-carbon double bond per molecule (that is, they are polyunsaturated), the result is usually described as partially hydrogenated vegetable oil; that is some, but usually not all, of the carbon-carbon double bonds in each molecule have been reduced. This is done by restricting the amount of hydrogen (or reducing agent) allowed to react with the fat.

Hydrogenation results in the conversion of liquid vegetable oils to solid or semi-solid fats, such as those present in margarine. Changing the degree of saturation of the fat changes some important physical properties such as the melting range, which is why liquid oils become semi-solid. Solid or semi-solid fats are preferred for baking because the way the fat mixes with flour produces a more desirable texture in the baked product. Because partially hydrogenated vegetable oils are cheaper than animal source fats, they are available in a wide range of consistencies, and have other desirable characteristics (e.g., increased oxidative stability/longer shelf life), they are the predominant fats used as shortening in most commercial baked goods.

Health implications

A side effect of incomplete hydrogenation having implications for human health is the isomerization of some of the remaining unsaturated carbon bonds. The cis configuration of these double bonds predominates in the unprocessed fats in most edible fat sources, but incomplete hydrogenation partially converts these molecules to trans isomers, which have been implicated in circulatory diseases including heart disease. The conversion from cis to trans bonds is favored because the trans configuration has lower energy than the natural cis one. At equilibrium, the trans/cis isomer ratio is about 2:1. Food legislation in the US and codes of practice in EU have long required labels declaring the fat content of foods in retail trade and, more recently, have also required declaration of the trans fat content. Trans fats are banned in Denmark and New York City.

Hydrogenation of coal

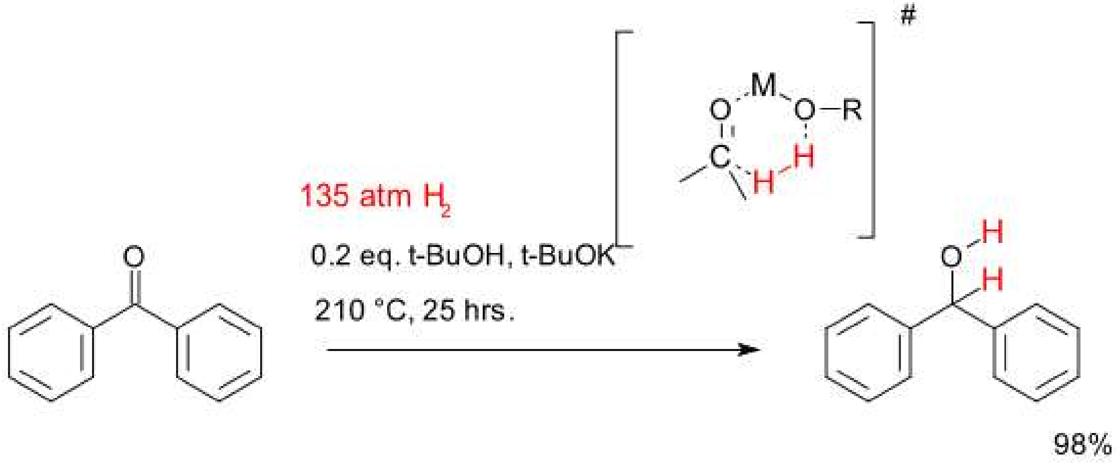
History

The earliest hydrogenation is that of platinum catalyzed addition of hydrogen to oxygen in the Döbereiner's lamp, a device commercialized as early as 1823. The French chemist Paul Sabatier is considered the father of the hydrogenation process. In 1897, building on the earlier work of James Boyce, an American chemist working in the manufacture of soap products, he discovered that the introduction of a trace of nickel as a catalyst facilitated the addition of hydrogen to molecules of gaseous hydrocarbons in what is now known as the Sabatier process. For this work Sabatier shared the 1912 Nobel Prize in Chemistry. Wilhelm Normann was awarded a patent in Germany in 1902 and in Britain in 1903 for the hydrogenation of liquid oils, which was the beginning of what is now a world wide industry. The commercially important Haber-Bosch process, first described in 1905, involves hydrogenation of nitrogen. In the Fischer-Tropsch process, reported in 1922 carbon monoxide, which is easily derived from coal, is hydrogenated to liquid fuels.

Also in 1922, Voorhees and Adams described an apparatus for performing hydrogenation under pressures above one atmosphere. The Parr shaker, the first product to allow hydrogenation using elevated pressures and temperatures, was commercialized in 1926 based on Voorhees and Adams' research and remains in widespread use. In 1924 Murray Raney developed a nickel fine powder catalyst named after him which is still widely used in hydrogenation reactions such as conversion of nitriles to amines or the production of margarine. In 1938, Otto Roelen described the oxo process which involves the addition of both hydrogen and carbon monoxide to alkenes, giving aldehydes. Since this process entails C-C coupling, it and its many variations remains highly topical into the new decade. The 1960s witnessed the development of homogeneous catalysts, e.g., Wilkinson's catalyst. In the 1980s, the Noyori asymmetric hydrogenation represented one of the first applications of hydrogenation in asymmetric synthesis, a growing application in the production of fine chemicals.

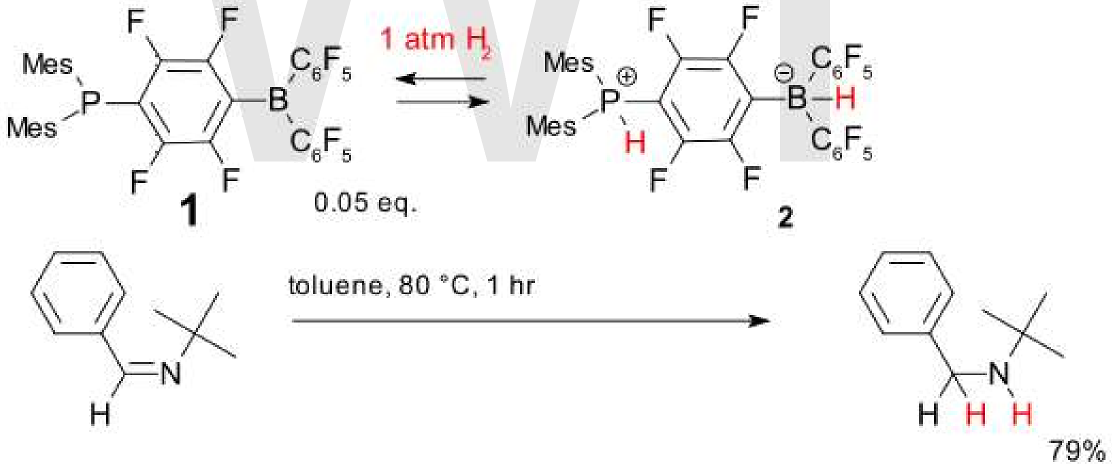
Metal-free hydrogenation

For all practical purposes, hydrogenation requires a metal catalyst. Hydrogenation can, however, proceed from some hydrogen donors without catalysts, illustrative hydrogen donors being diimide and aluminium isopropoxide. Some metal-free catalytic systems have been investigated in academic research. One such system for reduction of ketones consists of *tert*-butanol and potassium tert-butoxide and very high temperatures. The reaction depicted below describes the hydrogenation of benzophenone:



A chemical kinetics study found this reaction is first-order in all three reactants suggesting a cyclic 6-membered transition state.

Another system for metal-free hydrogenation is based on the phosphine-borane, compound **1**, which has been called a *frustrated Lewis pair*. It reversibly accepts dihydrogen at relatively low temperatures to form the phosphonium borate **2** which can reduce simple hindered imines.



The reduction of nitrobenzene to aniline has been reported to be catalysed by fullerene, its mono-anion, atmospheric hydrogen and UV light.

Equipment used for hydrogenation

Today's bench chemist has three main choices of hydrogenation equipment:

- Batch hydrogenation under atmospheric conditions
- Batch hydrogenation at elevated temperature and/or pressure

- Flow hydrogenation

Batch hydrogenation under atmospheric conditions

The original and still a commonly practised form of hydrogenation in teaching laboratories, this process is usually effected by adding solid catalyst to a round bottom flask of dissolved reactant which has been evacuated using nitrogen or argon gas and sealing the mixture with a penetrable rubber seal. Hydrogen gas is then supplied from a H_2-filled balloon. The resulting three phase mixture is agitated to promote mixing. Hydrogen uptake can be monitored, which can be useful for monitoring progress of a hydrogenation. This is achieved by either using a graduated tube containing a coloured liquid, usually aqueous copper sulfate or with gauges for each reaction vessel.

Batch hydrogenation at elevated temperature and/or pressure

Since many hydrogenation reactions such as hydrogenolysis of protecting groups and the reduction of aromatic systems proceed extremely sluggishly at atmospheric temperature and pressure, pressurised systems are popular. In these cases, catalyst is added to a solution of reactant under an inert atmosphere in a pressure vessel. Hydrogen is added directly from a cylinder or built in laboratory hydrogen source, and the pressurized slurry is mechanically rocked to provide agitation or a spinning basket is used. Heat may also be used, as the pressure compensates for the associated reduction in gas solubility.

Flow hydrogenation

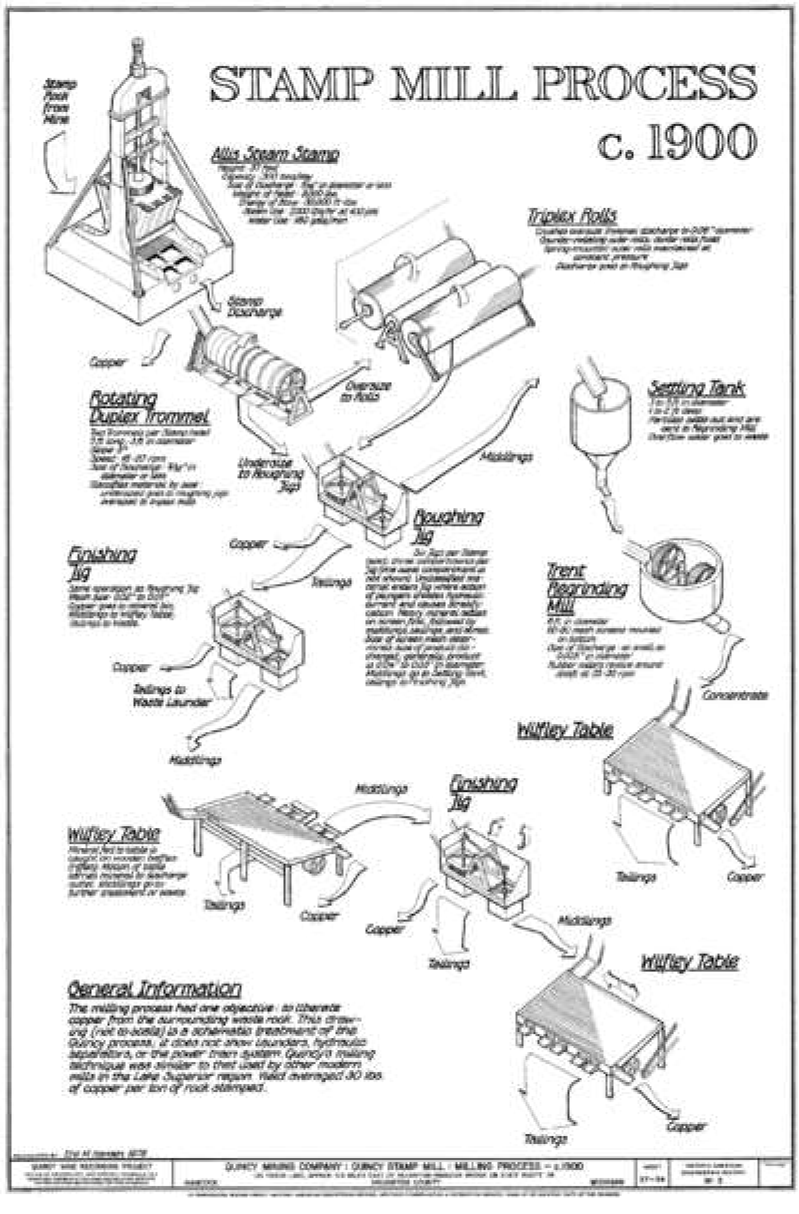
Flow hydrogenation has become a popular technique at the bench and increasingly the process scale. This technique involves continuously flowing a dilute stream of dissolved reactant over a fixed bed catalyst in the presence of hydrogen. Using established HPLC technology, this technique allows the application of pressures from atmospheric to 1,450 PSI. Elevated temperatures may also be used. At the bench scale, systems use a range of pre-packed catalysts which eliminates the need for weighing and filtering pyrophoric catalysts.

Industrial reactors

Catalytic hydrogenation is done in a tubular plug-flow reactor (PFR) packed with a supported catalyst. The pressures and temperatures are typically high, although this depends on the catalyst. Catalyst loading is typically much lower than in laboratory batch hydrogenation, and various promoters are added to the metal, or mixed metals are used, to improve activity, selectivity and catalyst stability. The use of nickel is common despite its low activity, due to its low cost compared to precious metals.

Chapter- 5

Unit Operation



An ore extraction process broken into its constituent unit operations (Quincy Mine, Hancock, MI ca. 1900)

In chemical engineering and related fields, a **unit operation** is a basic step in a process. For example in milk processing, homogenization, pasteurization, chilling, and packaging are each unit operations which are connected to create the overall process. A process may have many unit operations to obtain the desired product.

Historically, the different chemical industries were regarded as different industrial processes and with different principles. Arthur Dehon Little propounded the concept of "unit operations" to explain industrial chemistry processes in 1916. In 1923, William H.Walker, Warren K. Lewis and William H. McAdams wrote the book *The Principles of Chemical Engineering* and explained the variety of chemical industries have processes which follow the same physical laws. They summed-up these similar processes into unit operations. Each unit operation follows the same physical laws and may be used in all chemical industries. The unit operations form the fundamental principles of chemical engineering.

Chemical engineering unit operations consist of five classes:

1. Fluid flow processes, including fluids transportation, filtration, solids fluidization
2. Heat transfer processes, including evaporation, condensation
3. Mass transfer processes, including gas absorption, distillation, extraction, adsorption, drying
4. Thermodynamic processes, including gas liquefaction, refrigeration
5. Mechanical processes, including solids transportation, crushing and pulverization, screening and sieving

Chemical engineering unit operations also fall in the following categories:

- Combination (mixing)
- Separation (distillation)
- Reaction (chemical reaction)

Chemical engineering unit operations and chemical engineering unit processing form the main principles of all kinds of chemical industries and are the foundation of designs of chemical plants, factories, and equipment used.

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.

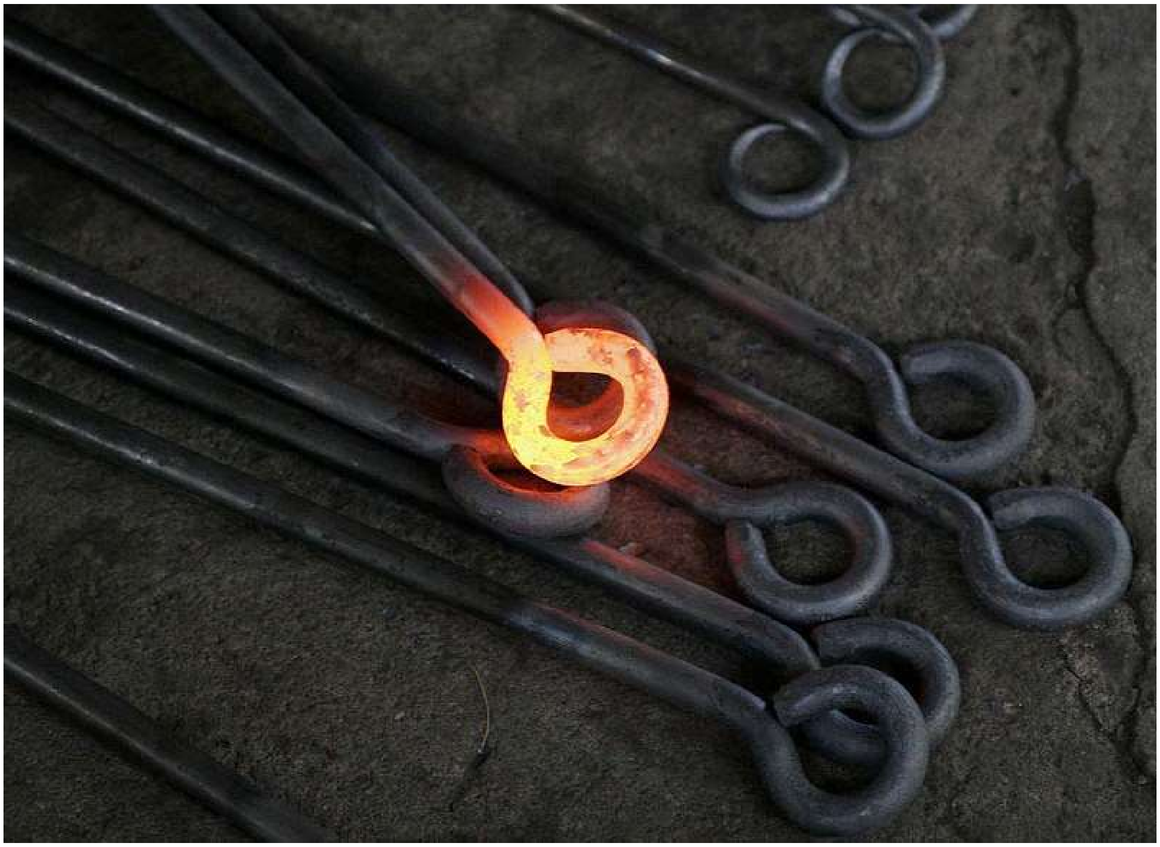
Convection

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.

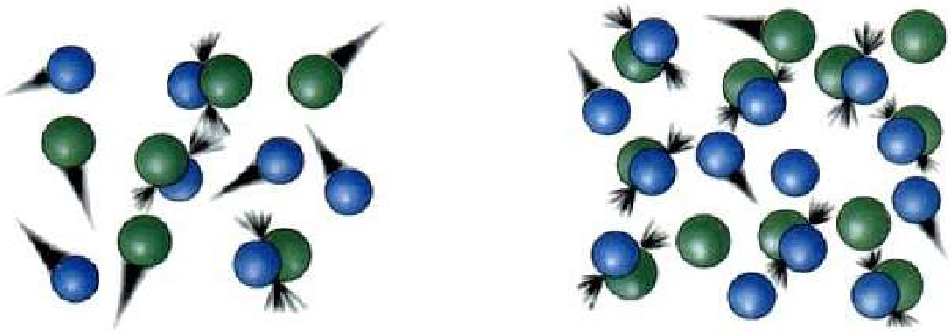
A thermocouple is a junction between two different metals that produces a voltage related to a temperature difference. Thermocouples are a widely used type of temperature sensor for measurement and control, and can also be used to convert heat into electric power.

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- 6

Chemical Kinetics



Low concentration = Few collisions High concentration = More collisions

Reaction rate tends to increase with concentration - a phenomenon explained by collision theory.

Chemical kinetics, also known as **reaction kinetics**, is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero-order reactions (for which reaction rates are independent of concentration), first-order reactions, and second-order reactions, and can be derived for others. In consecutive reactions the rate-determining step often determines the kinetics. In consecutive first-order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.

Factors affecting reaction rate

Nature of the reactants

Depending upon what substances are reacting, the reaction rate varies. Acid/base reactions, the formation of salts, and ion exchange are fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be very slow. Nature and strength of bonds in reactant molecules greatly influences the rate of its transformation into products. The reactions which involve lesser bond rearrangement proceed faster than the reactions which involve larger bond rearrangement.

Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in different phases, the reaction is limited to the interface between the reactants. Reaction can only occur at their area of contact, in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant, the greater its surface area per unit volume, and the more contact it makes with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches—one doesn't start with large logs right away. In organic chemistry, On water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions.

Concentration

Concentration plays a very important role in reactions, because according to the collision theory of chemical reactions, molecules must collide in order to react together. As the concentration of the reactants increases, the frequency of the molecules colliding increases, striking each other more frequently by being in closer contact at any given point in time. Think of two reactants being in a closed container. All the molecules contained within are colliding constantly. By increasing the amount of one or more of the reactants it causes these collisions to happen more often, increasing the reaction rate.

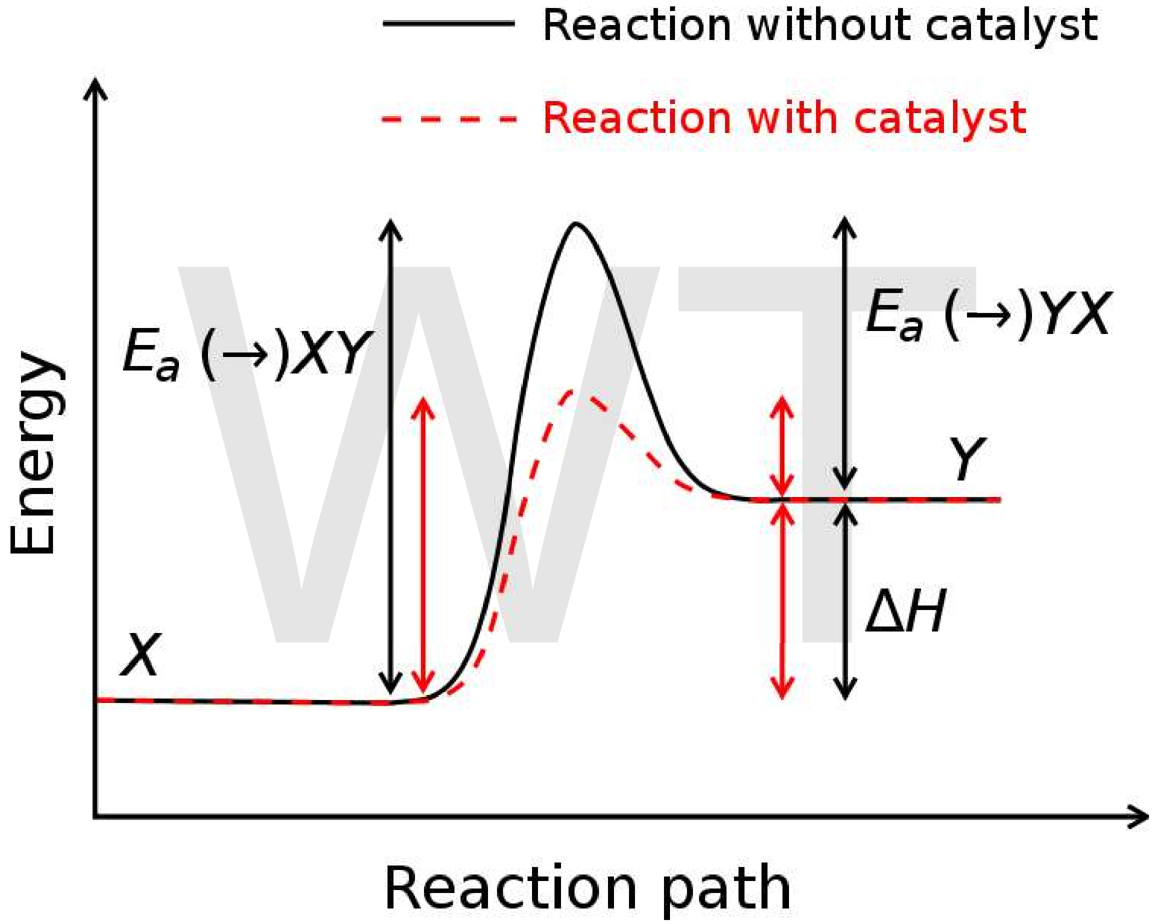
Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the Q_{10} (temperature coefficient) is often between 1.5 and 2.5.

A reaction's kinetics can also be studied with a temperature jump approach. This involves using a sharp rise in temperature and observing the relaxation rate of an equilibrium process.

Catalysts



Generic potential energy diagram showing the effect of a catalyst in an hypothetical endothermic chemical reaction. 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.

A catalyst is a substance that accelerates the rate of a chemical reaction but remains chemically unchanged afterwards. The catalyst increases rate reaction by providing a different reaction mechanism to occur with a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis-Menten kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibria, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation.

Agitating or mixing a solution will also accelerate the rate of a chemical reaction, as this gives the particles greater kinetic energy, increasing the number of collisions between reactants and therefore the possibility of successful collisions.

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

Equilibrium

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber–Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov–Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.

Free energy

In general terms, the free energy change (ΔG) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two different products, the thermodynamically most stable one will generally form except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin–Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a different product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships.

The kinetic isotope effect is the difference in the rate of a chemical reaction when an atom in one of the reactants is replaced by one of its isotopes.

Chemical kinetics provides information on residence time and heat transfer in a chemical reactor in chemical engineering and the molar mass distribution in polymer chemistry.

Applications

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the complex chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.

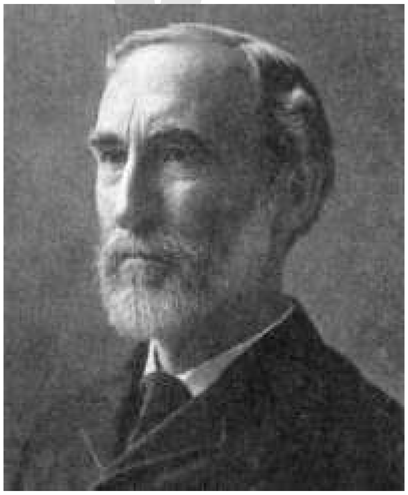
Chapter- 7

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 $\Delta U_{f\,\mathrm{reactants}}^{\circ}$ 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 $\Delta U_{f\,\mathrm{products}}^{\circ}$ 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 (though not assessed in the same way as a hydrocarbon fuel).

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 dG 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 dG 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*

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

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 dG 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 $\pm PdV$. 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 PdV 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- 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.

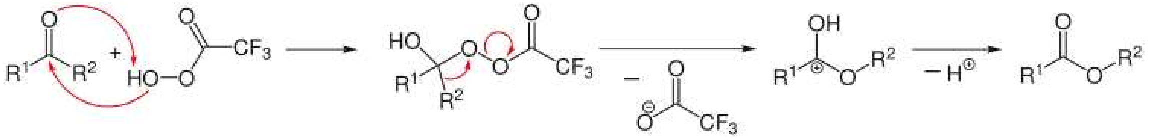
Regarding the organic chemistry, it was long believed that compounds obtained from living organisms were too complex to be obtained synthetically. According to the concept of vitalism, organic matter was endowed with a "vital force" and distinguished from inorganic materials. This separation was ended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

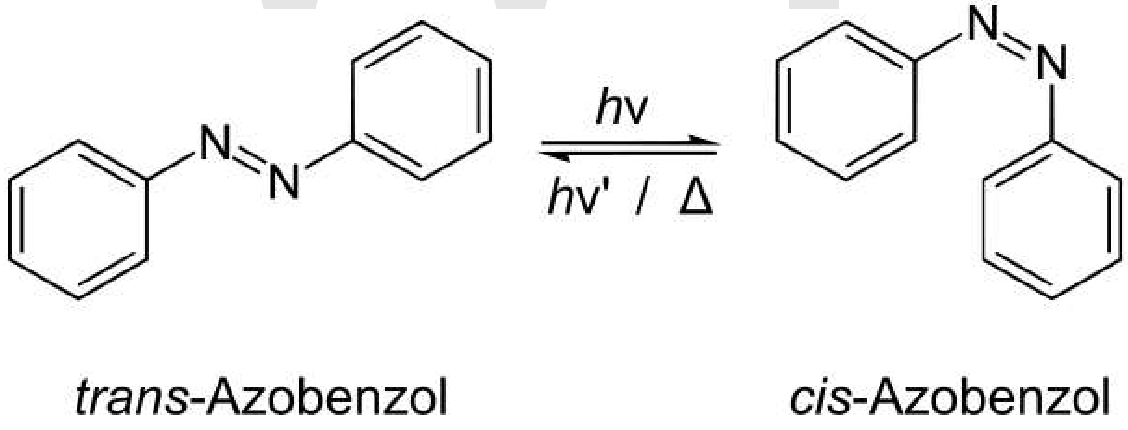


An example of organic reaction: oxidation of ketones to esters with peroxycarboxylic acid

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:

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

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

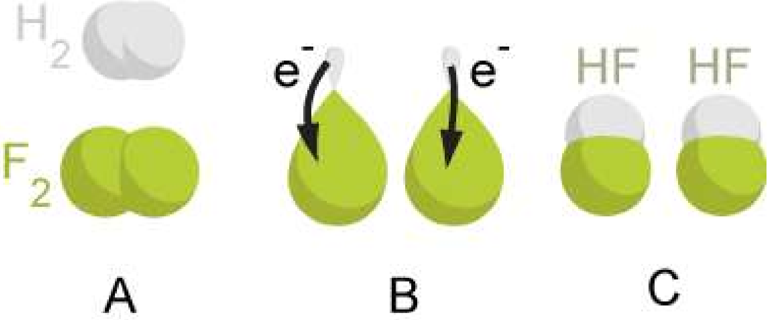
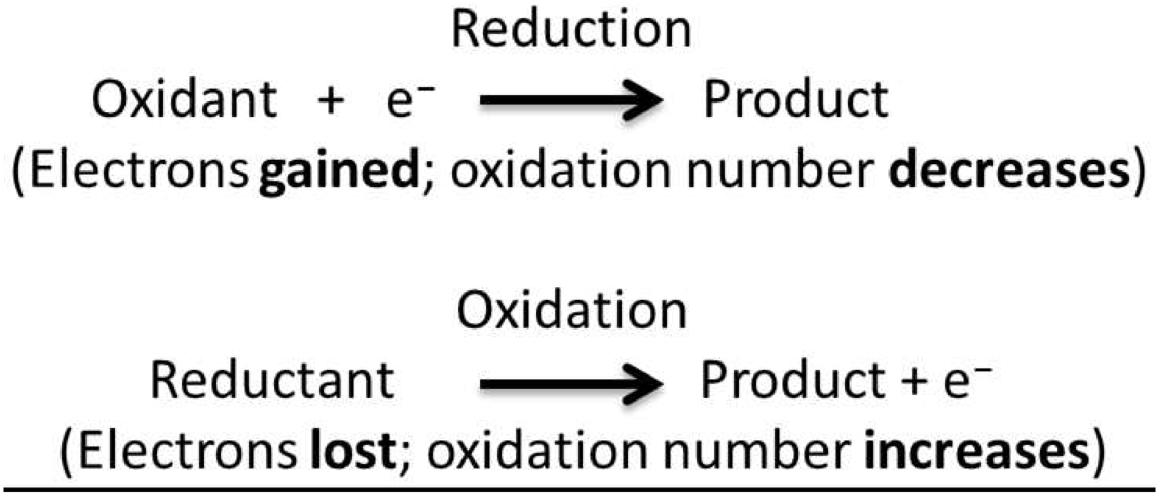


Illustration of a redox reaction



Reduction

$$\text{Oxidant} + e^- \longrightarrow \text{Product}$$

(Electrons **gained**; oxidation number **decreases**)

Oxidation

$$\text{Reductant} \longrightarrow \text{Product} + e^-$$

(Electrons **lost**; oxidation number **increases**)

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:

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

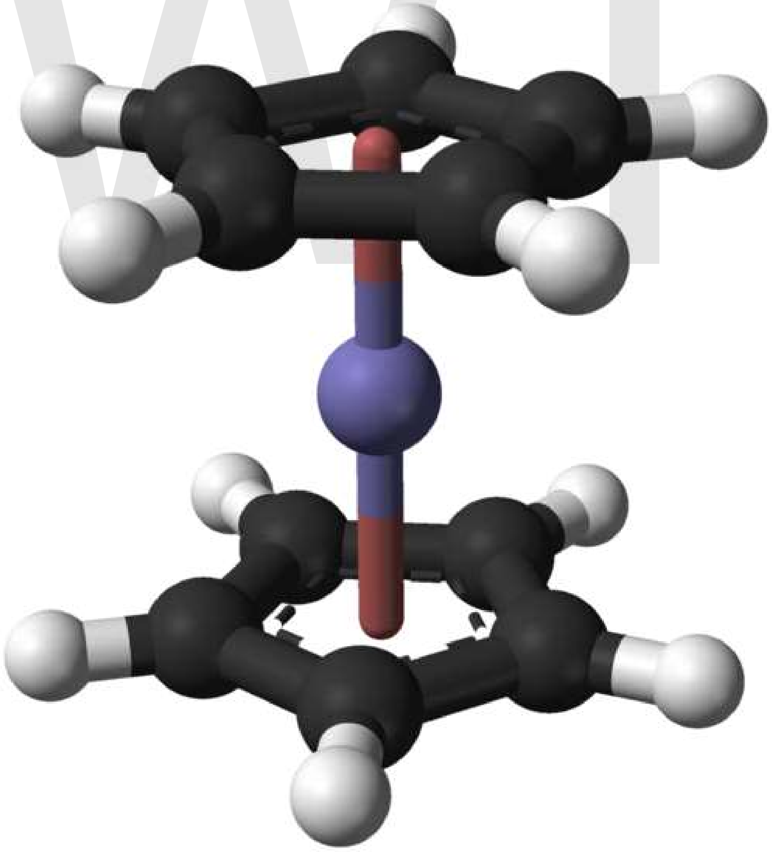
Here I_2 is reduced to I^- and $S_2O_3{}^{2-}$ (thiosulfate anion) is oxidized to $S_4O_6{}^{2-}$.

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.

$$\mathrm{HA} + \mathrm{B} \rightleftharpoons \mathrm{A}^- + \mathrm{HB}^+$$

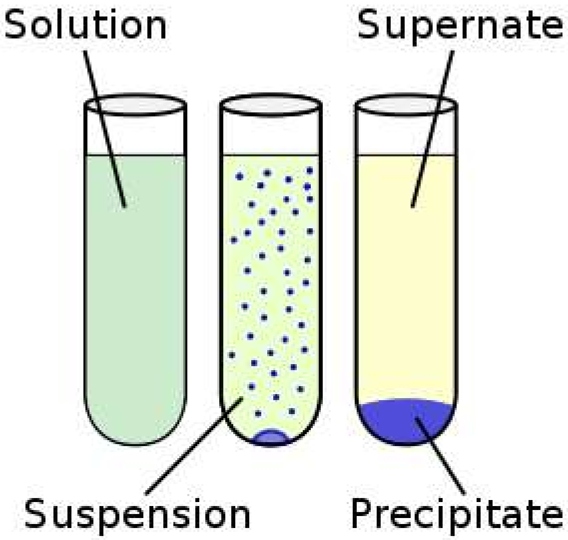
Acid-base reaction, HA: acid, B: Base, A^-: conjugated base, HB^+: conjugated acid

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

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

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

Precipitation



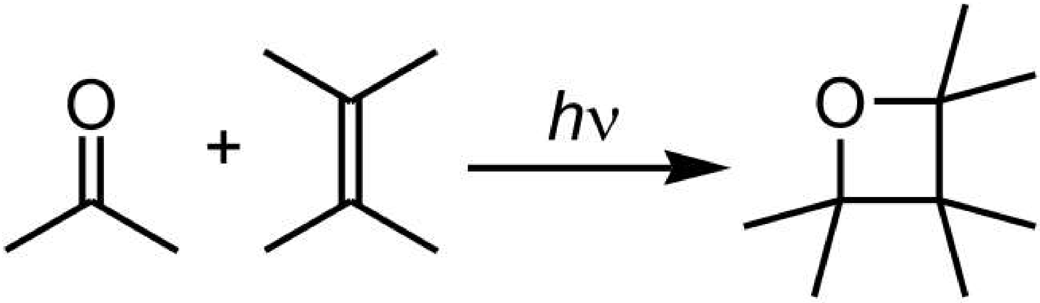
Precipitation

Precipitation is the formation of a solid in a solution or inside another solid during a chemical reaction. It usually takes place when the concentration of dissolved ions exceeds the solubility limit and forms an insoluble salt. This process can be assisted by adding a precipitating agent or by removal of the solvent. Rapid precipitation results in an amorphous or microcrystalline residue and slow process can yield single crystals. The latter can also be obtained by recrystallization from microcrystalline salts.

Solid-state reactions

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

Photochemical reactions

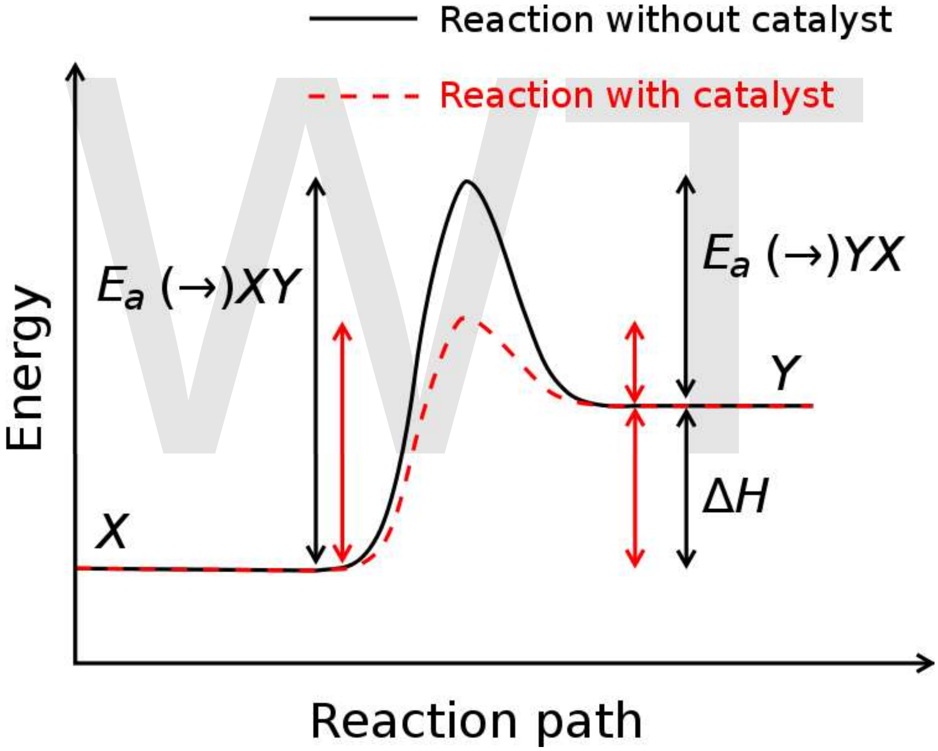


In this Paterno–Büchi reaction, a photoexcited carbonyl group is added to an unexcited olefin, yielding an oxetane.

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

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

Catalysis



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

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

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

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

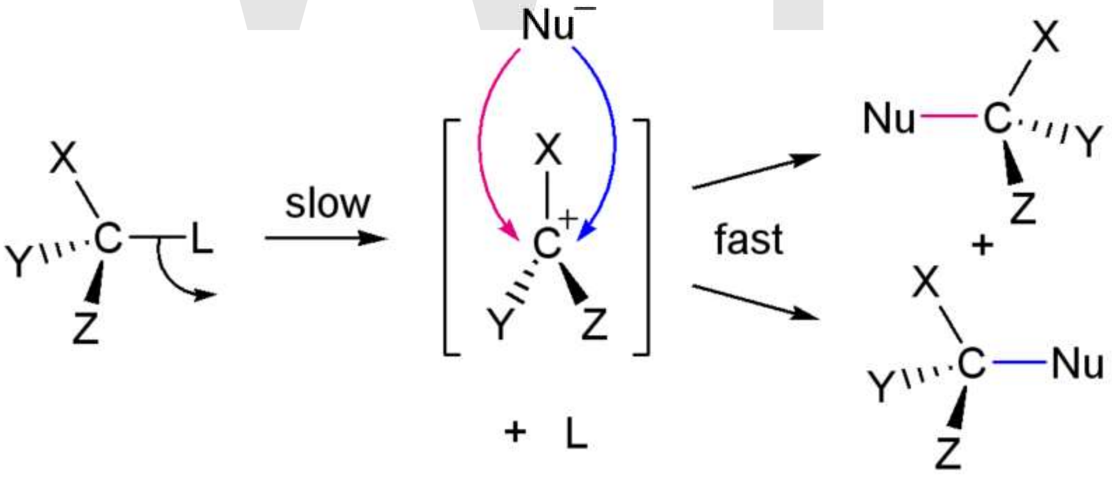
Reactions in organic chemistry

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

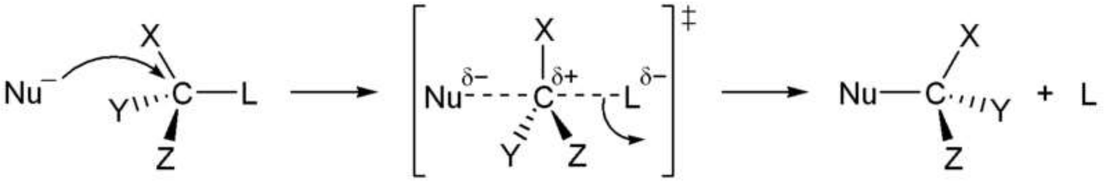
Substitution

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

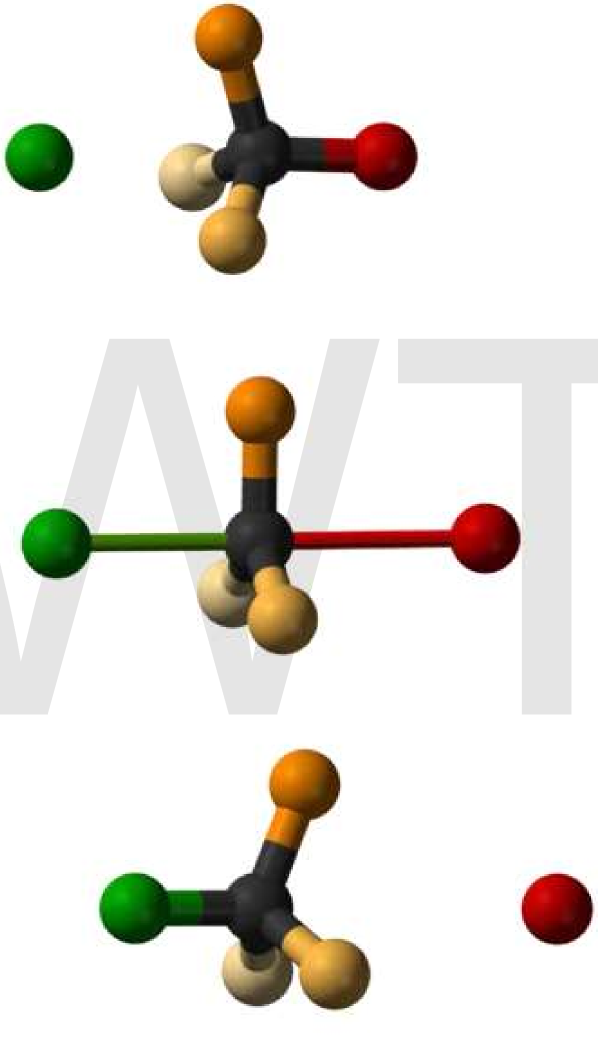
In the first type, a nucleophile, an atom or molecule with an excess of electrons and thus a negative charge or partial charge, replaces another atom or part of the "substrate" molecule. The electron pair from the nucleophile attacks the substrate forming a new bond, while the leaving group departs with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



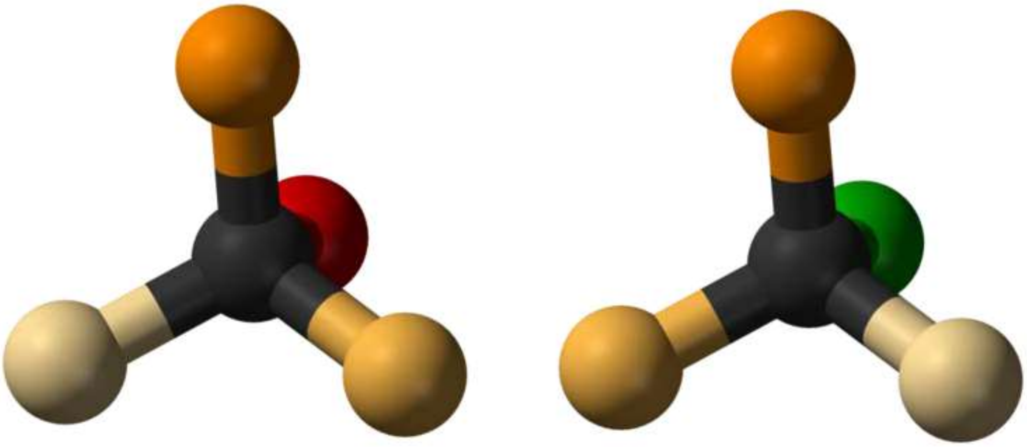
S_N1 mechanism



S_N2 mechanism



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

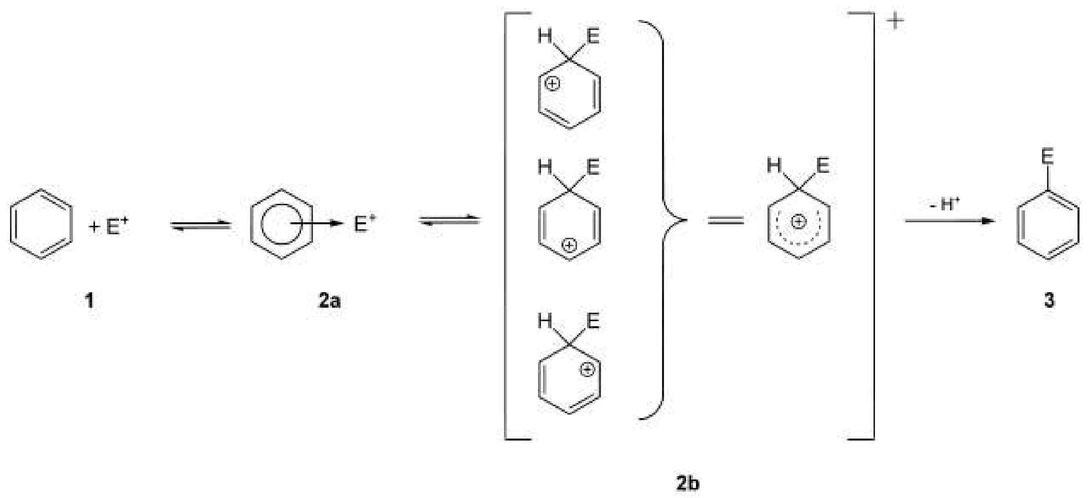


S_N2 reaction causes stereo inversion (Walden inversion)

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

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

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



Mechanism of electrophilic aromatic substitution

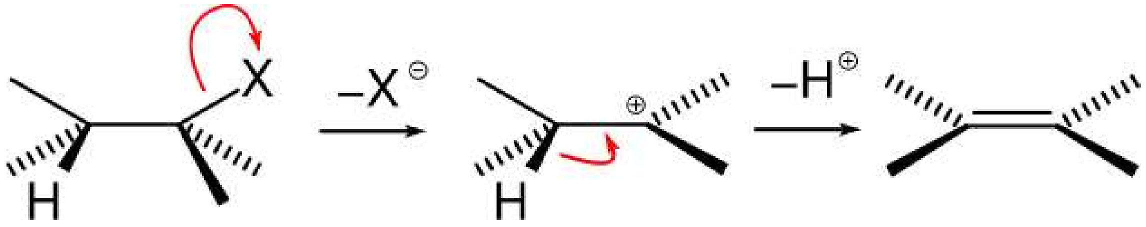
In the third type of substitution reaction, radical substitution, the attacking particle is a radical. This process usually takes the form of a chain reaction, for example in the reaction of alkanes with halogens. In the first step, light or heat disintegrates the halogen-containing molecules producing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

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

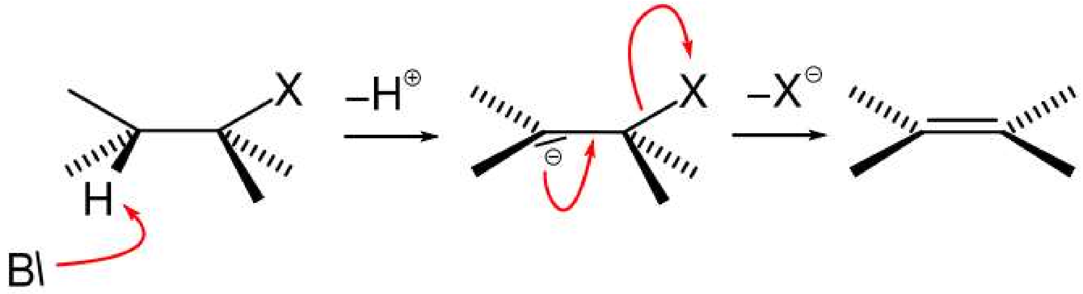
Reactions during the chain reaction of radical substitution

Addition and elimination

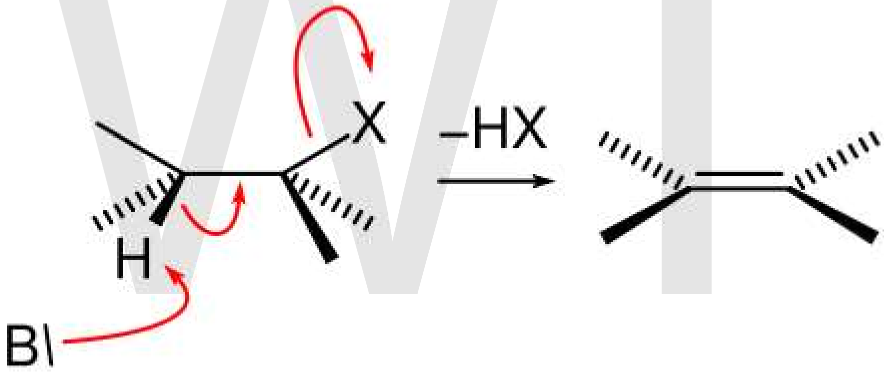
The addition and its counterpart, the elimination, are reactions which change the number of substituents on the carbon atom, and form or cleave multiple bonds. Double and triple bonds can be produced by eliminating a suitable leaving group. Similar to the nucleophilic substitution, there are several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

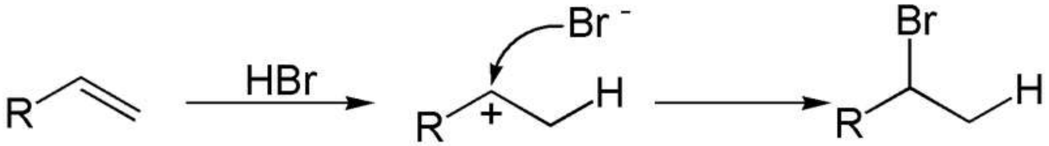


E1cb elimination



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.

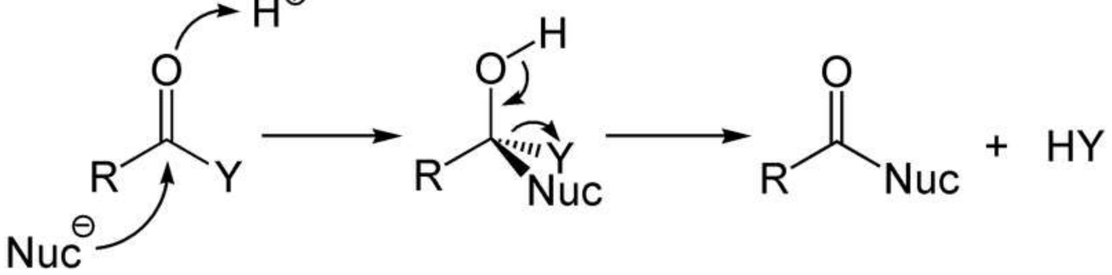


Electrophilic addition of hydrogen bromide

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.

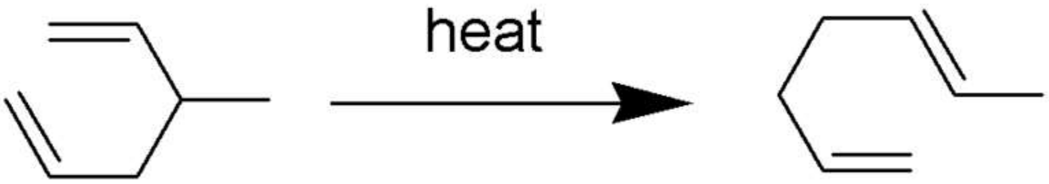


Acid-catalyzed addition-elimination mechanism

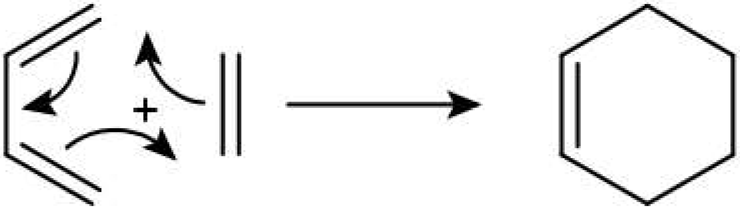
Nucleophilic addition of a carbanion or another nucleophile to the double bond of an alpha, beta unsaturated carbonyl compound can proceed via the Michael reaction, which belongs to the larger class of conjugate additions. This is one of the most useful methods for the mild formation of C-C bonds.

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.

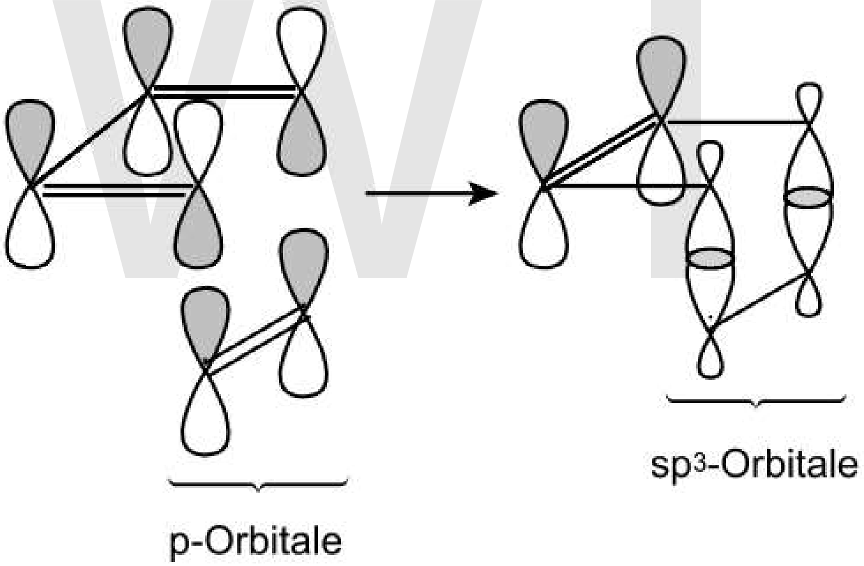
Other organic reaction mechanisms



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

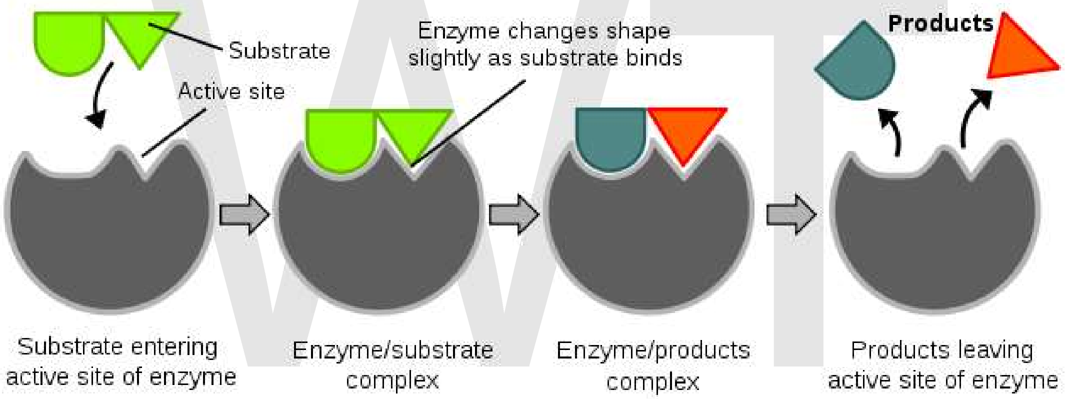


Illustration of the induced fit model of enzyme activity

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.

<table>
<tr><td rowspan="4">Continuum mechanics
The study of the physics of continuous materials</td><td rowspan="2">Solid mechanics
The study of the physics of continuous materials with a defined rest shape.</td><td colspan="2">Elasticity
Describes materials that return to their rest shape after an applied stress.</td></tr>
<tr><td>Plasticity
Describes materials that permanently deform after a sufficient applied stress.</td><td rowspan="2">Rheology
The study of materials with both solid and fluid characteristics.</td></tr>
<tr><td rowspan="2">Fluid mechanics
The study of the physics of continuous materials which take the shape of their container.</td><td>Non-Newtonian fluids</td></tr>
<tr><td colspan="2">Newtonian fluids</td></tr>
</table>

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.

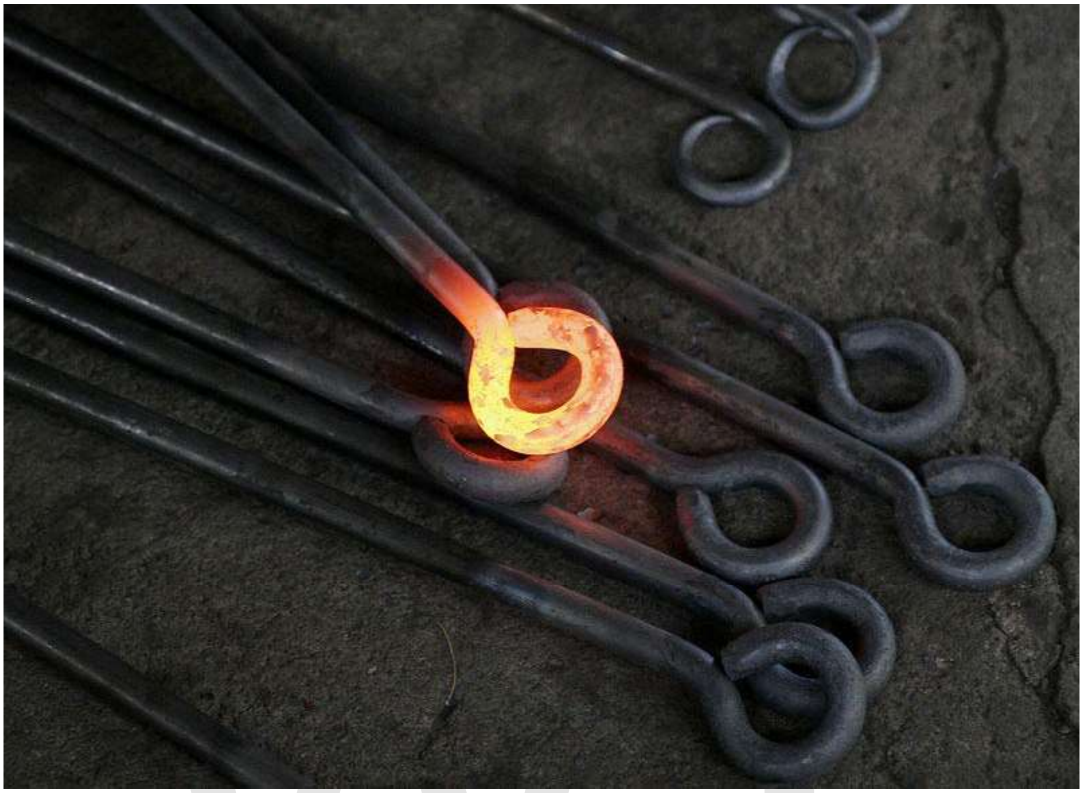
Convection

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/m²K. 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

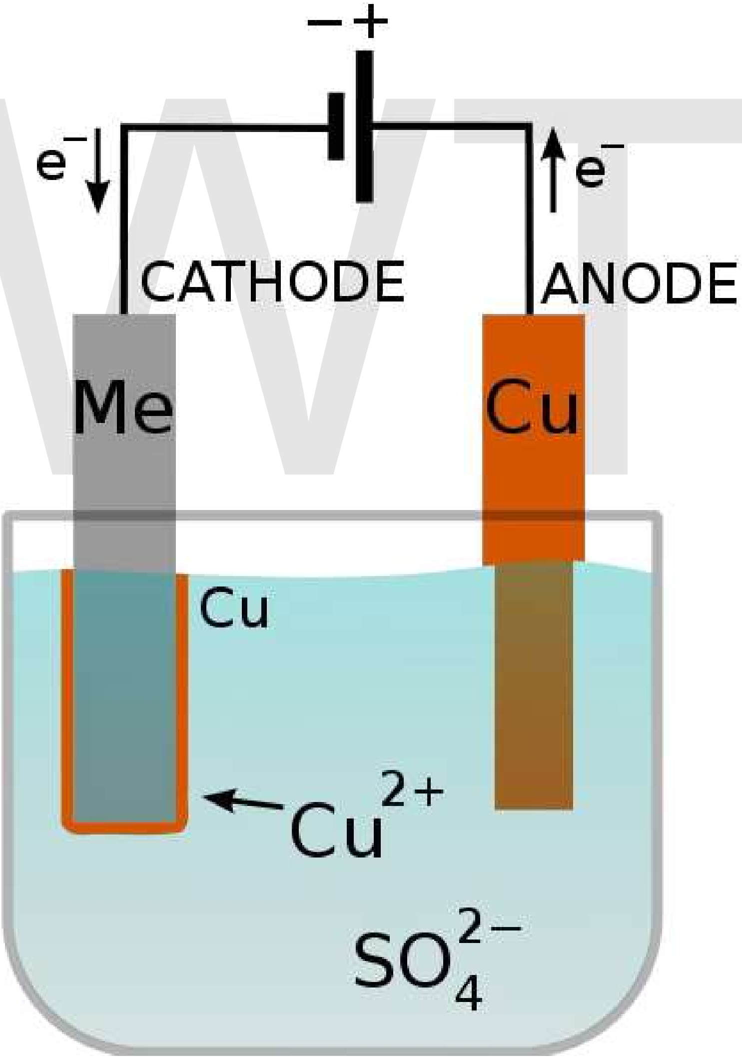
copper electroplating machine for layering PCBs

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.

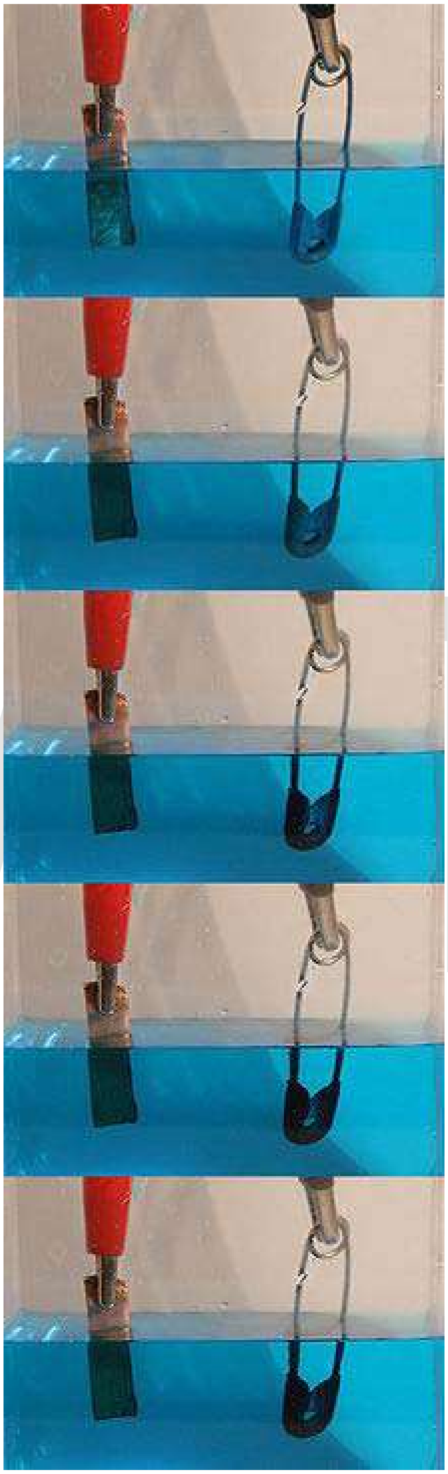
When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes.

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

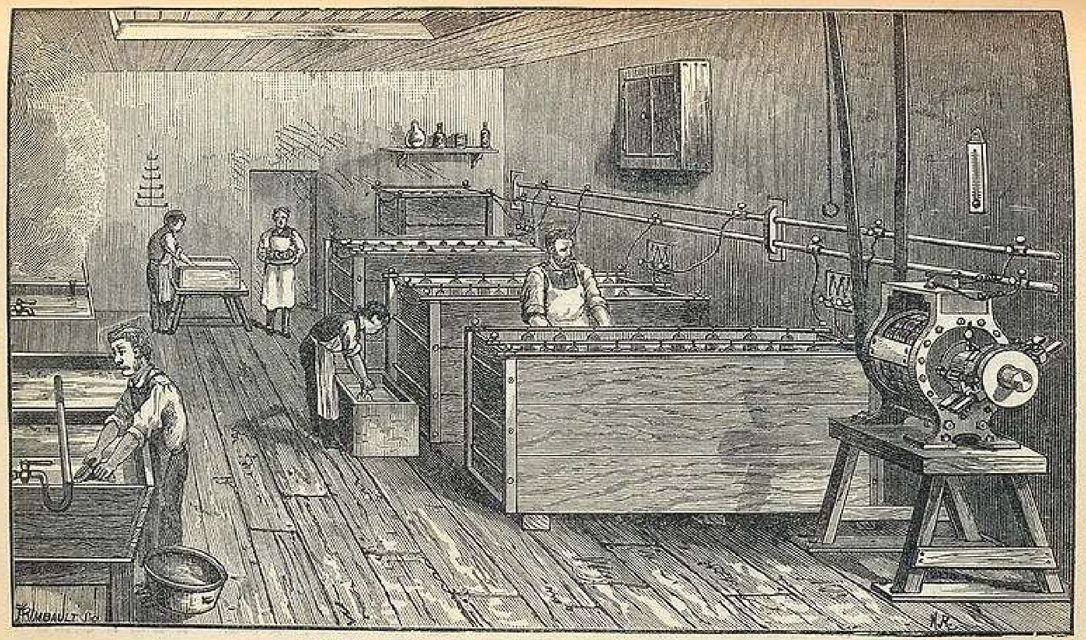


Fig. 108.—Nickel-plating by Dynamo-electricity.

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

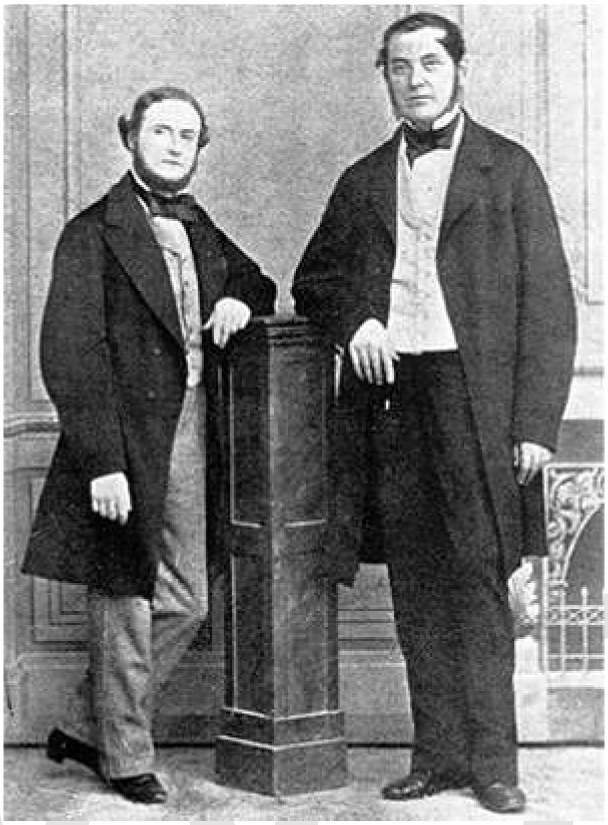
Analytical Chemistry

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.

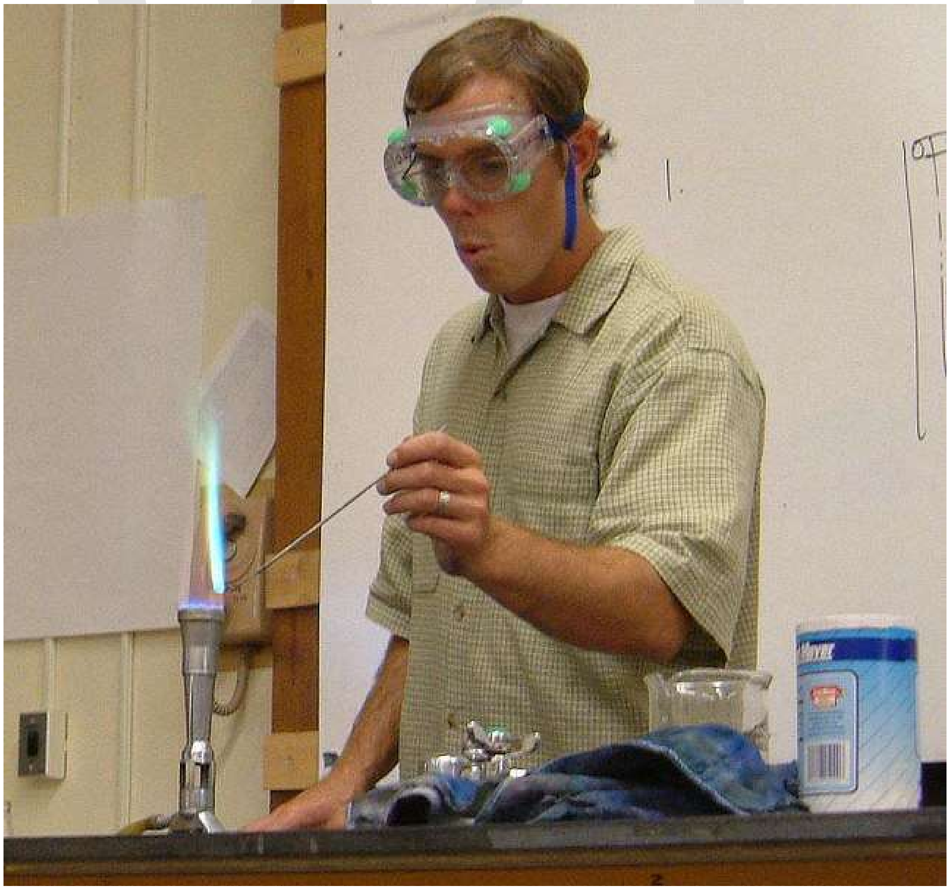
Most of the major developments in analytical chemistry take place after 1900. During this period instrumental analysis becomes progressively dominant in the field. In particular many of the basic spectroscopic and spectrometric techniques were discovered in the early 20th century and refined in the late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

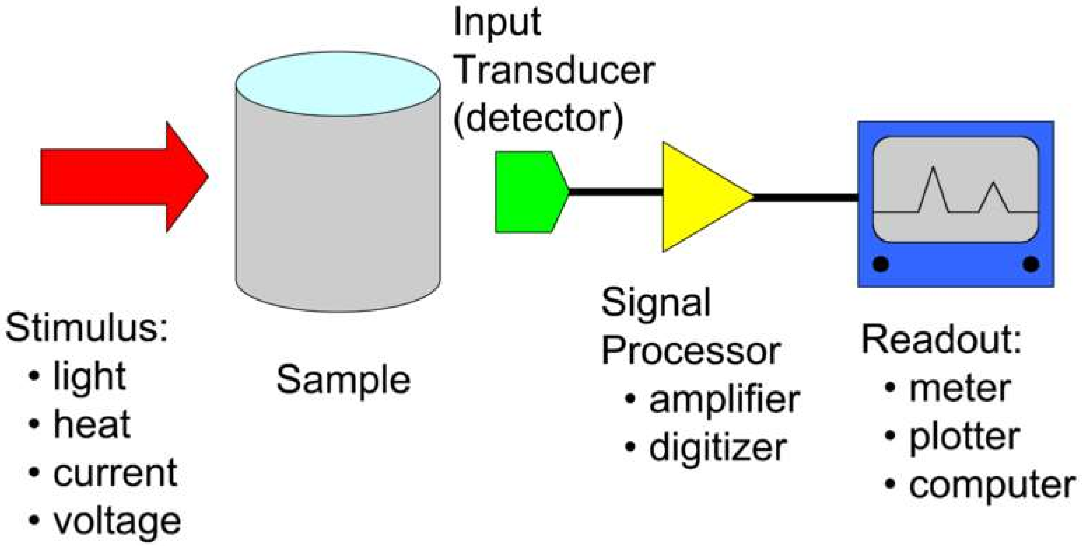
Gravimetric analysis

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.

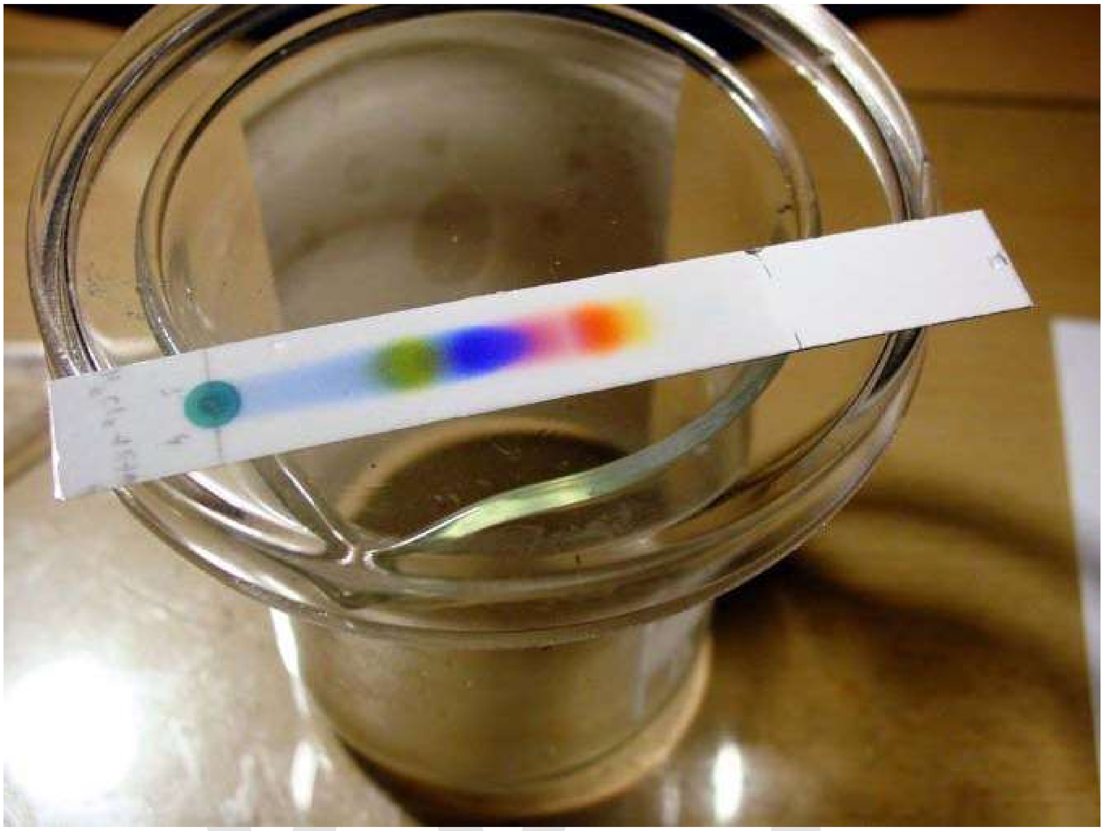
Electrochemical analysis

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.

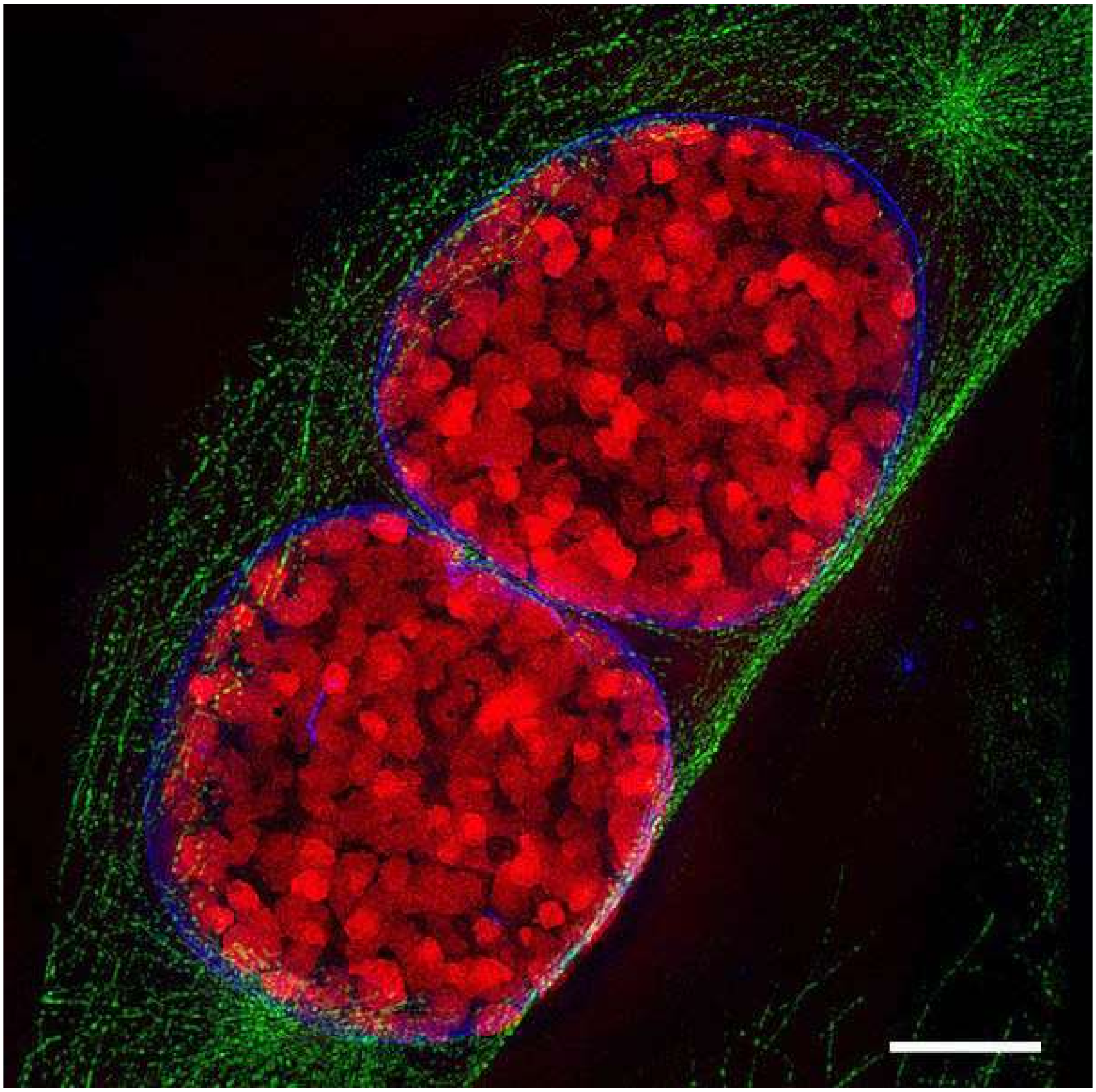
Separation processes are used to decrease the complexity of material mixtures. Chromatography and electrophoresis are representative of this field.

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.

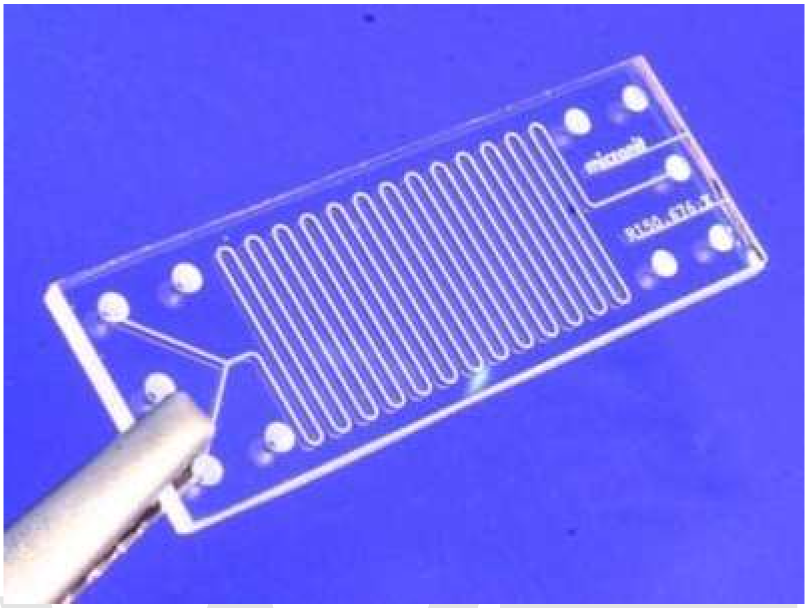
Microscopy



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

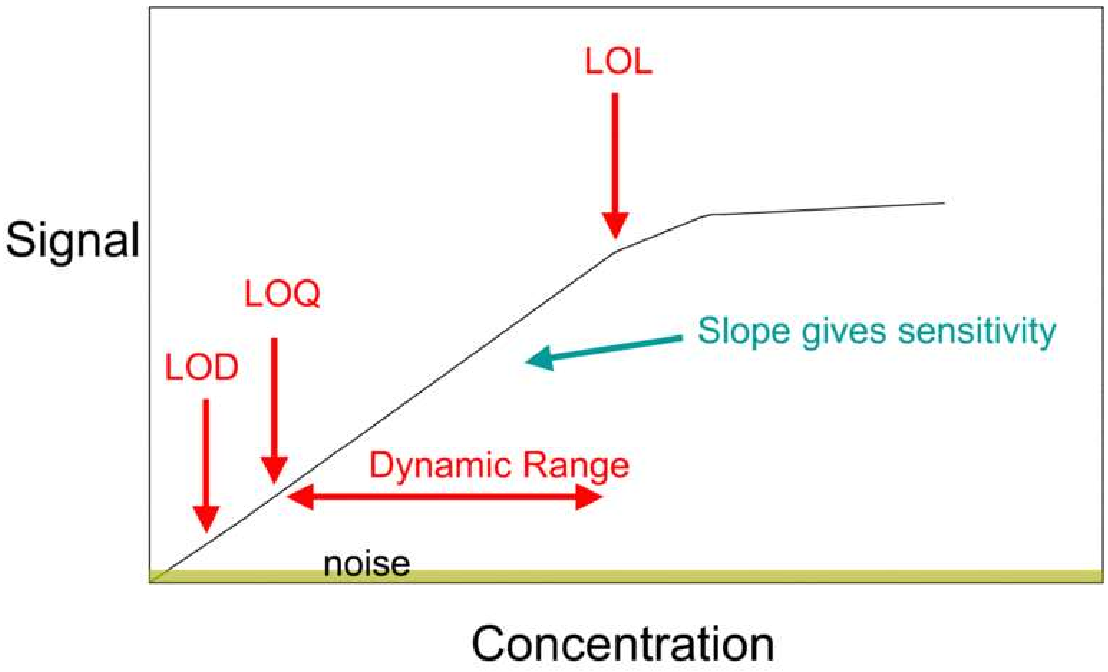


A glass microreactor

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

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

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

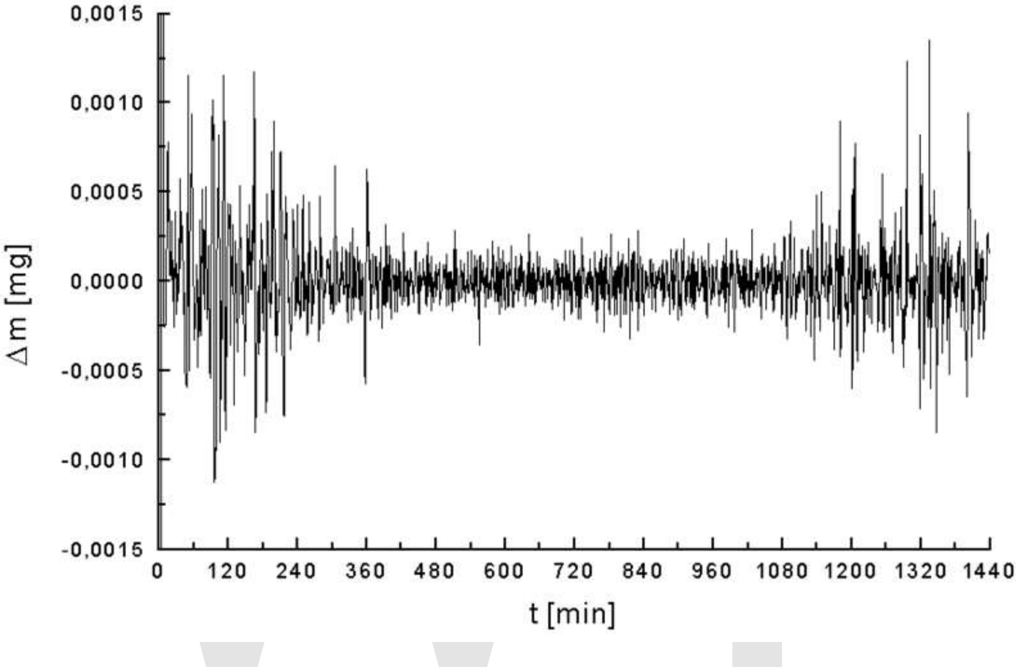
$$i_{RMS} = \sqrt{2\,e\,I\,\Delta f}$$

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.

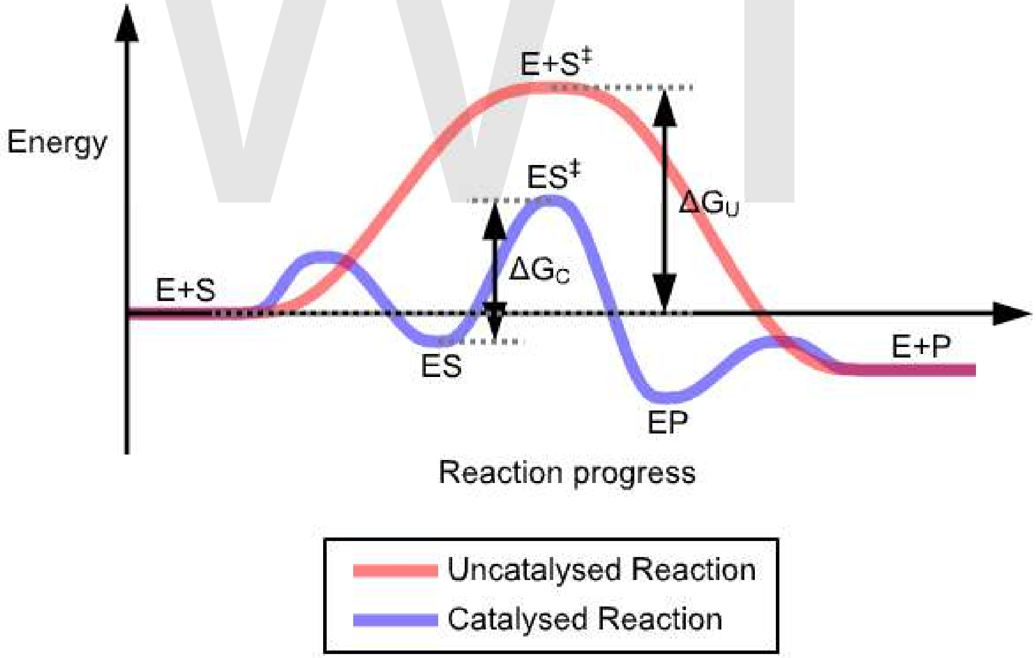
Among active contemporary analytical chemistry research fields, micro total analysis system is considered as a great promise of revolutionary technology. In this approach, integrated and miniaturized analytical systems are being developed to control and analyze single cells and single molecules. This 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

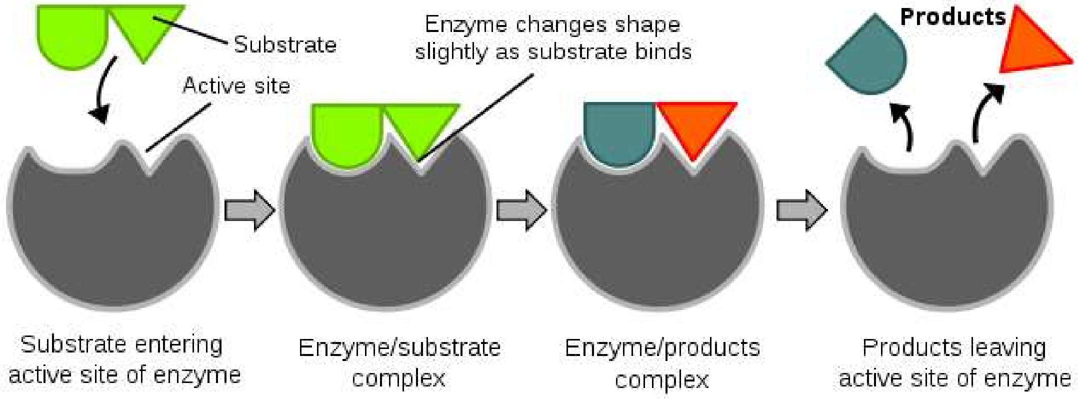
Enzyme catalysis is the catalysis of chemical reactions by specialized proteins known as enzymes. Catalysis of biochemical reactions in the cell is vital due to the very low reaction rates of the uncatalysed reactions.

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.

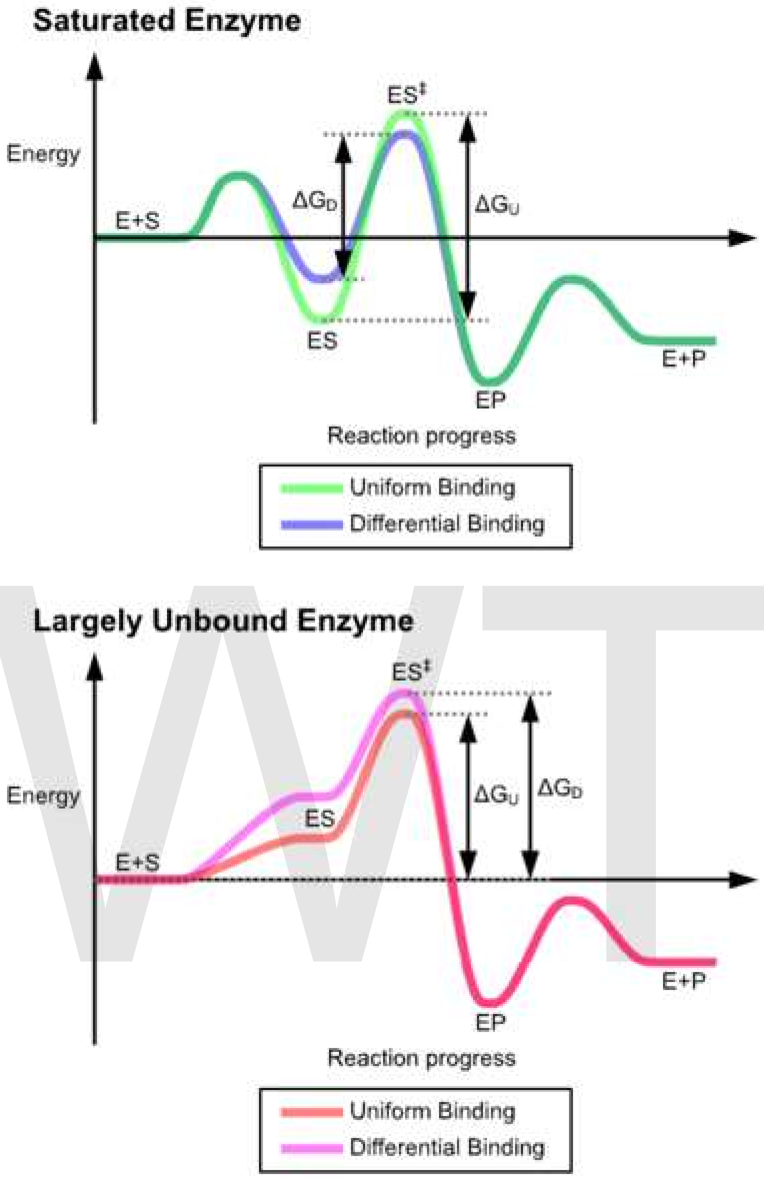
Induced fit



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

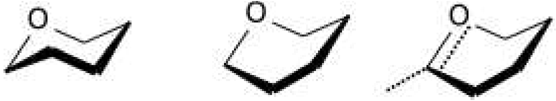
This is the principal effect of induced fit binding, where the affinity of the enzyme to the transition state is greater than to the substrate itself. This induces structural rearrangements which strain substrate bonds into a position closer to the conformation of the transition state, so lowering the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

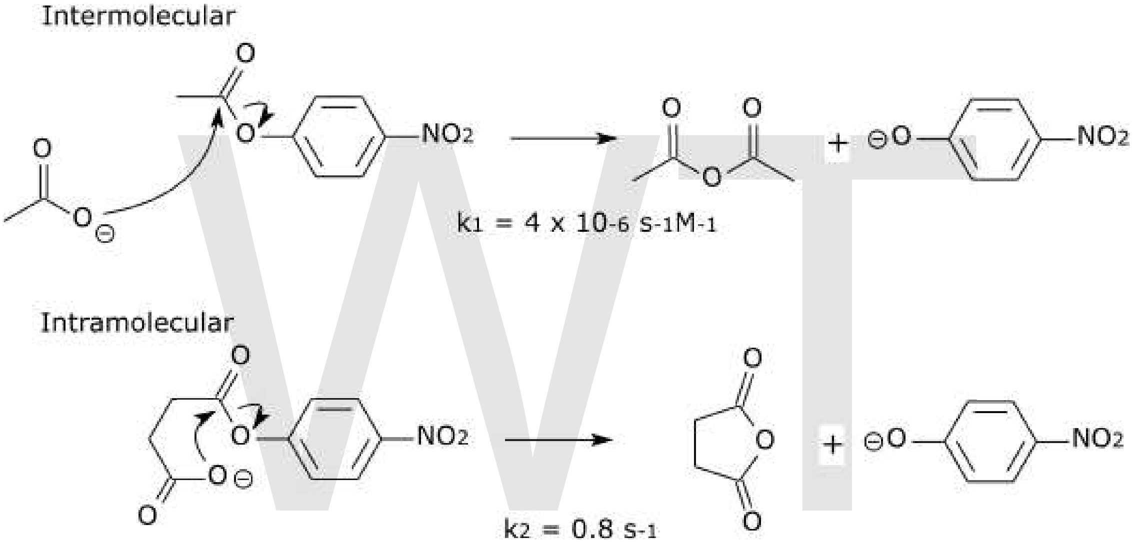
Catalysis by proximity and orientation

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.

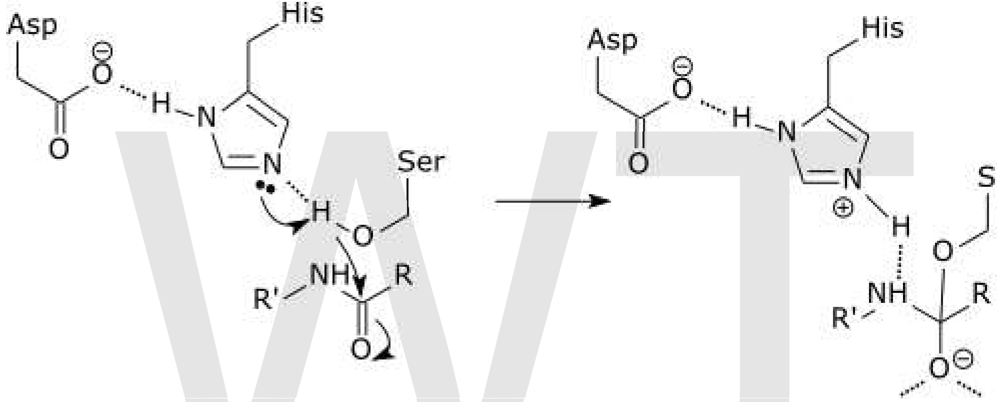
Many reaction mechanisms involving acid/base catalysis assume a substantially altered pKa. This alteration of pKa is possible through the local environment of the residue.

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.

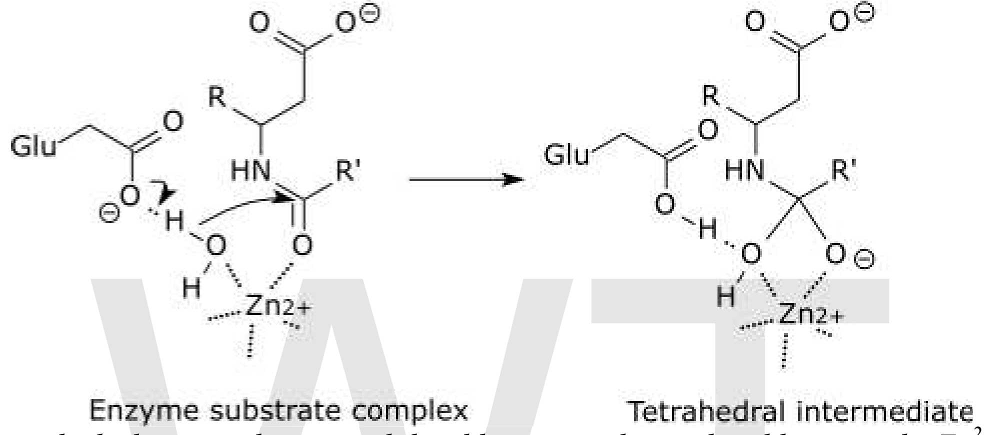
Electrostatic catalysis

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).