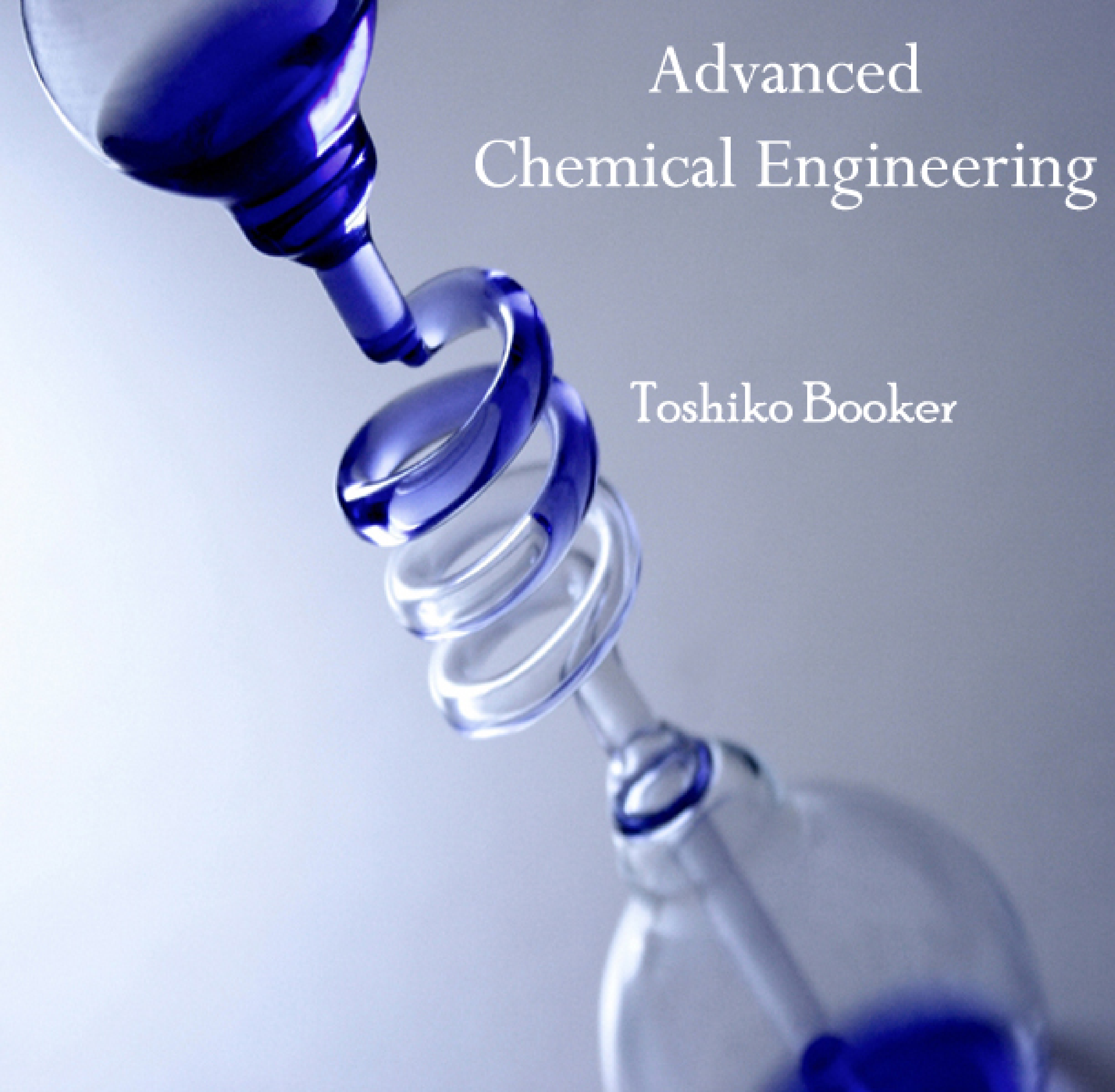

Advanced Chemical Engineering

Toshiko Booker

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Chapter- 1

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)

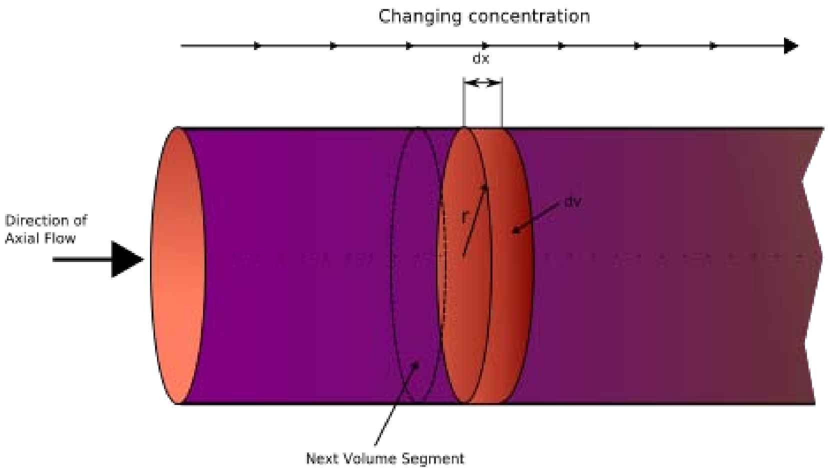
Reactor CSTR. Check of a condition of the case. Note the impeller (or agitator) blades on the shaft for mixing. Also note the baffle at the bottom of the image which also helps in mixing.

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.

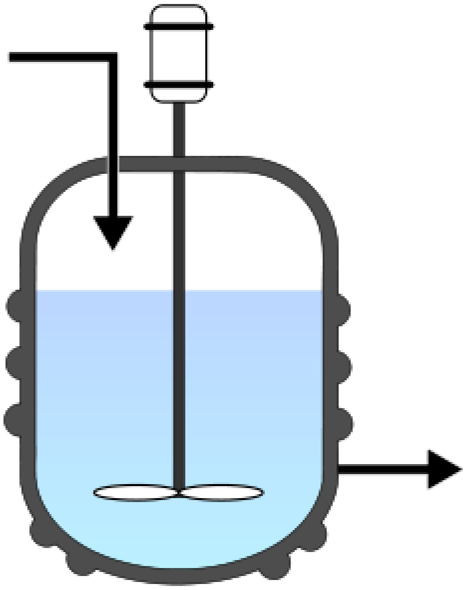
Catalytic reactor

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.

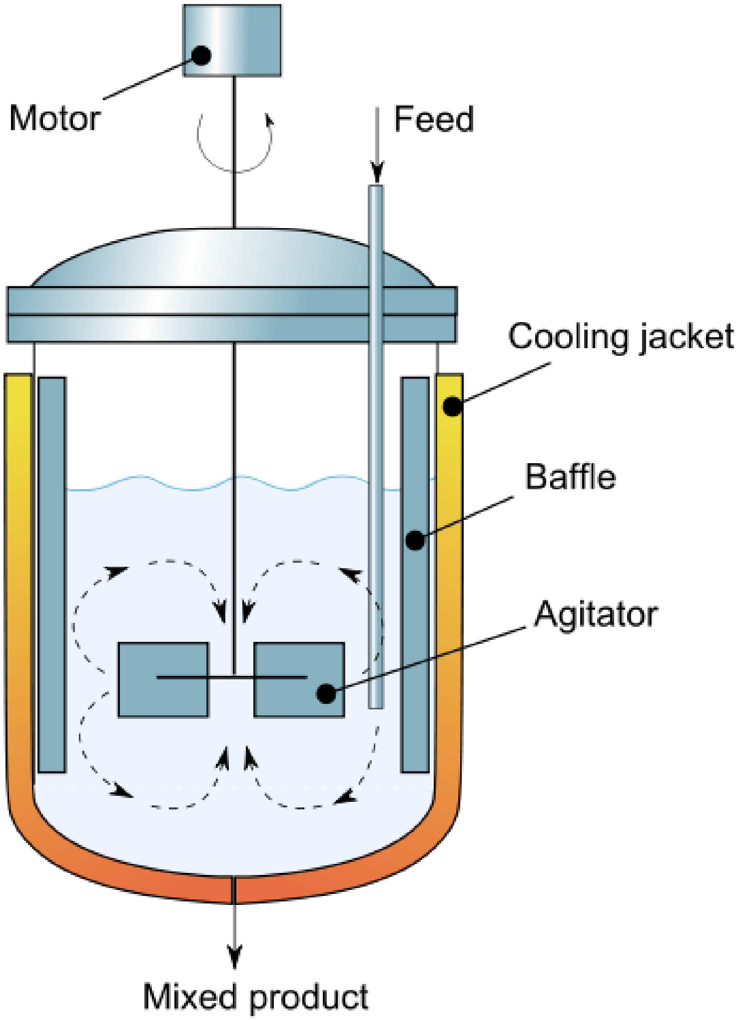
The behavior of a CSTR is often approximated or modeled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR). All calculations performed with CISTRs assume perfect mixing. In a perfectly mixed reactor, the output composition is identical to composition of the material inside the reactor, which 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.

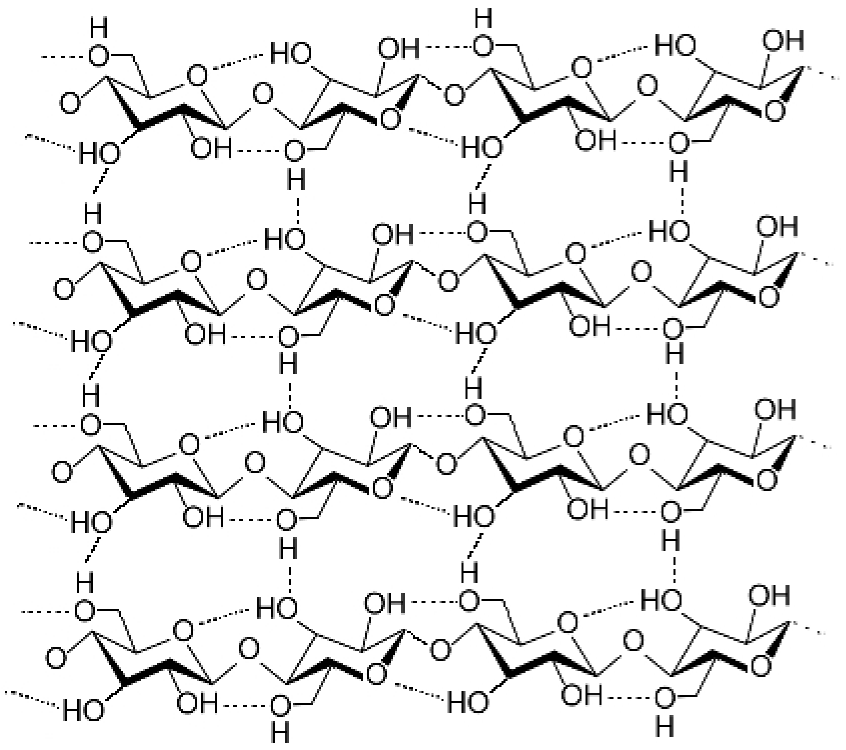
Product Recycling

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

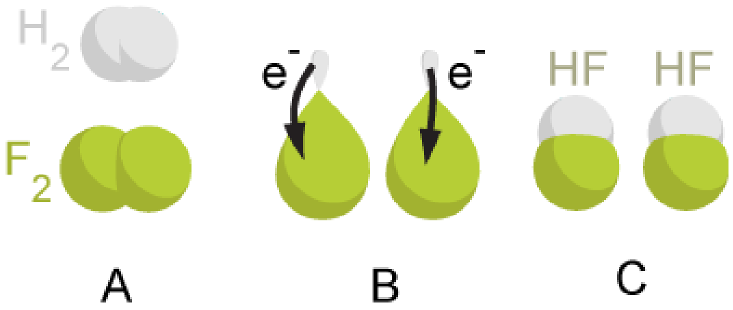


Illustration of a redox reaction

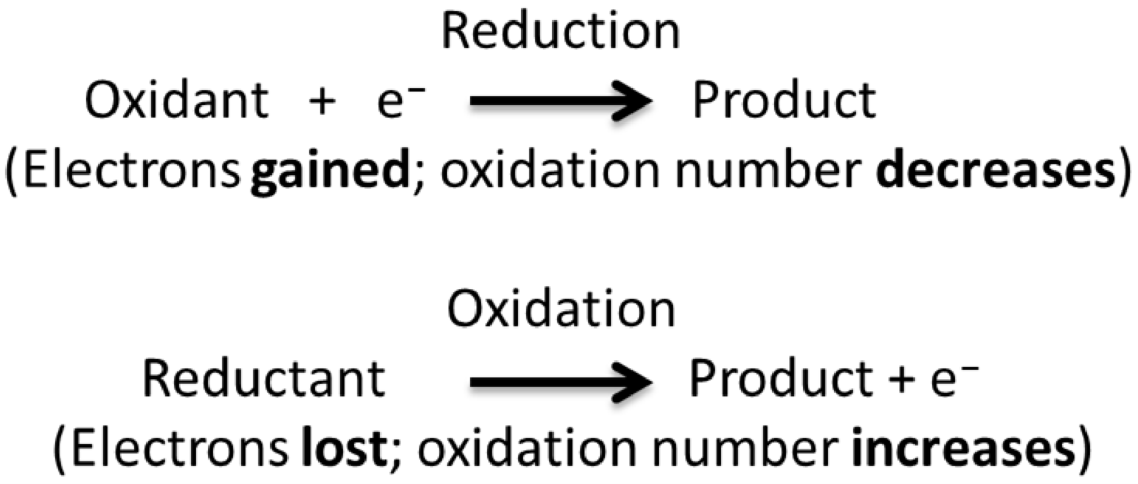
Redox (shorthand for **oxidation-reduction**) reactions describe all chemical reactions in which atoms have their oxidation number (oxidation state) changed. This can be either a simple redox process, such as the oxidation of carbon to yield carbon dioxide (CO_2) or the reduction of carbon by hydrogen 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.

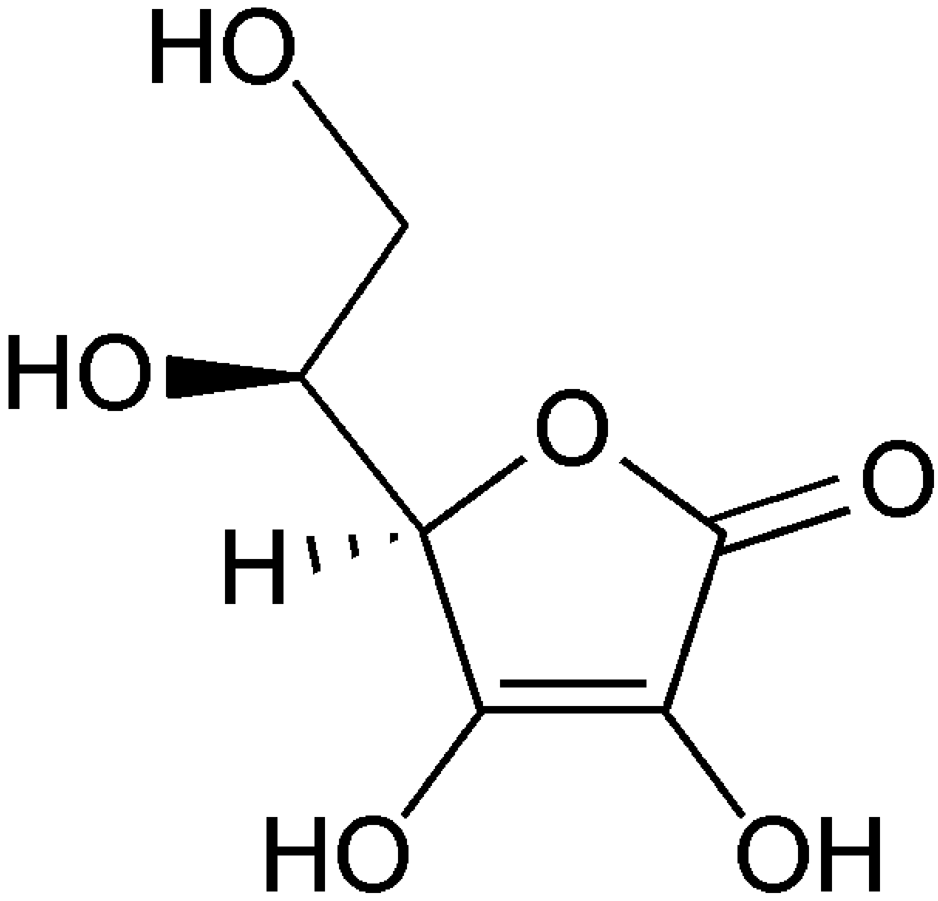
Oxidation is used in a wide variety of industries such as in the production of cleaning products and oxidizing ammonia to produce nitric acid, which is used in most fertilizers.

Redox reactions are the foundation of electrochemical cells.

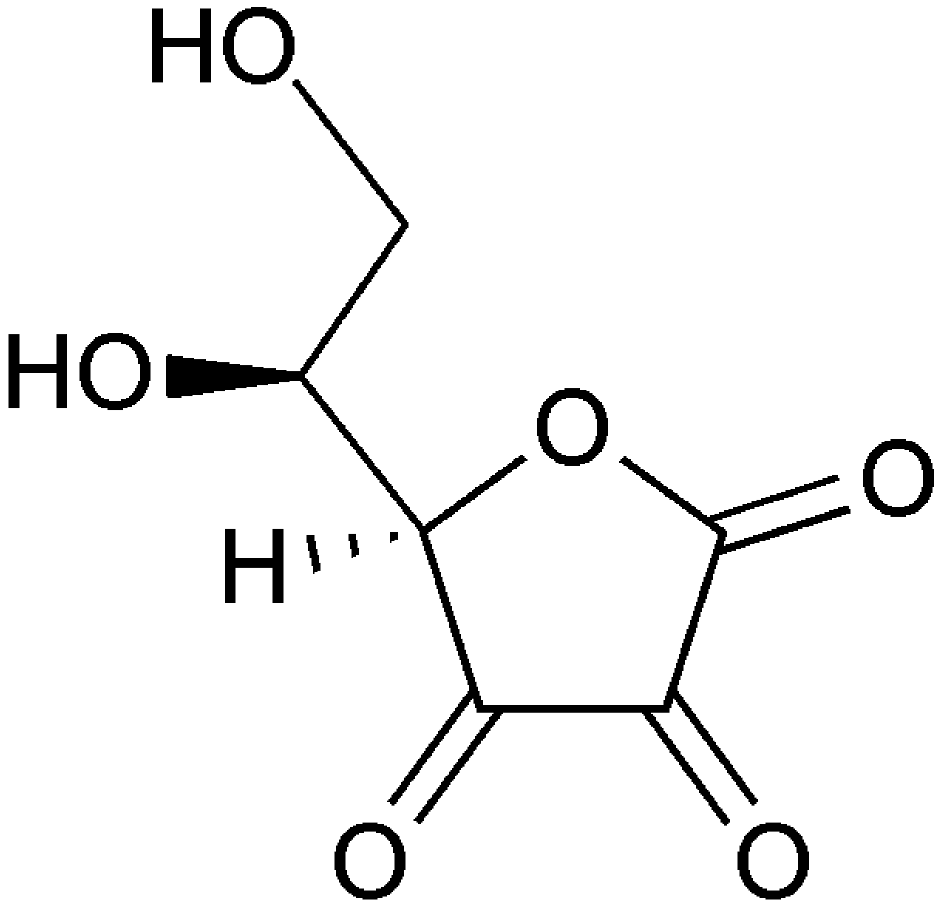
The process of electroplating uses redox reactions to coat objects with a thin layer of a material, as in chrome plated automotive parts, silver plating cutlery, and gold-plated jewelry.

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:

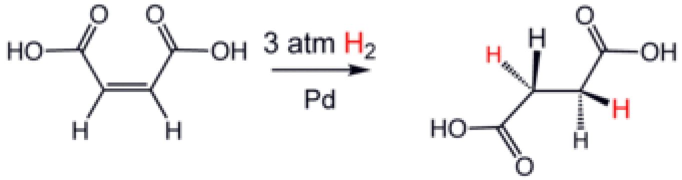
$$2\ KMnO_4 + 3\ Na_2SO_3 + H_2O \rightarrow 2\ MnO_2 + 3\ Na_2SO_4 + 2\ KOH$$

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:

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

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

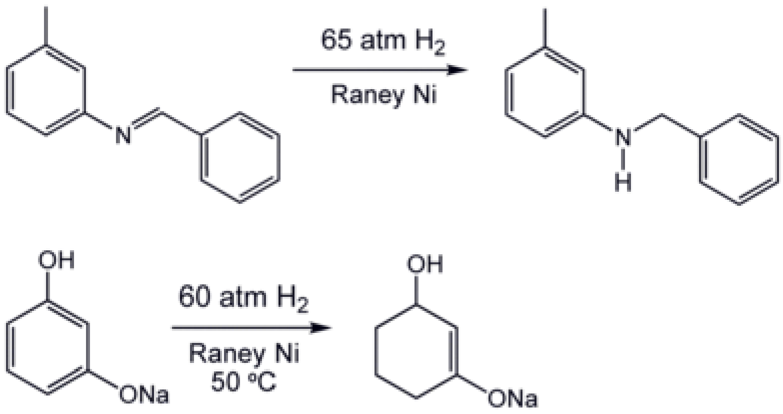
An important characteristic of alkene and alkyne hydrogenations, both the homogeneously and heterogeneously catalyzed versions, is that hydrogen addition occurs with "syn addition", with hydrogen entering from the least hindered side. Typical substrates are listed in the table

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

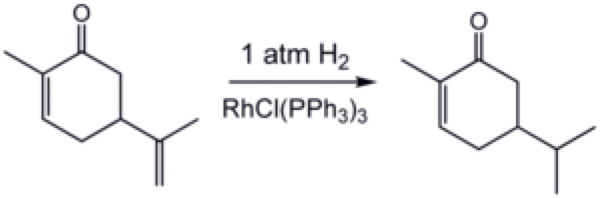
With rare exception, no reaction below 480 °F occurs between H_2 and organic compounds in the absence of metal catalysts. The catalyst binds *both* the H_2 and the unsaturated substrate and facilitates their union. Platinum group metals, particularly platinum, palladium, rhodium, and ruthenium, form 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:



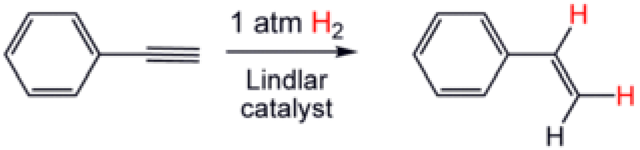
Hydrogenation is sensitive to steric hindrance explaining the selectivity for reaction with the exocyclic double bond but not the internal double bond.

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)

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

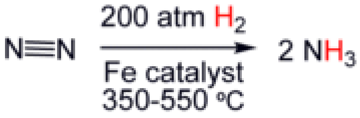
- transfer of the second hydrogen atom from the metal to the alkyl group with simultaneous dissociation of the alkane ("reductive elimination")

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

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

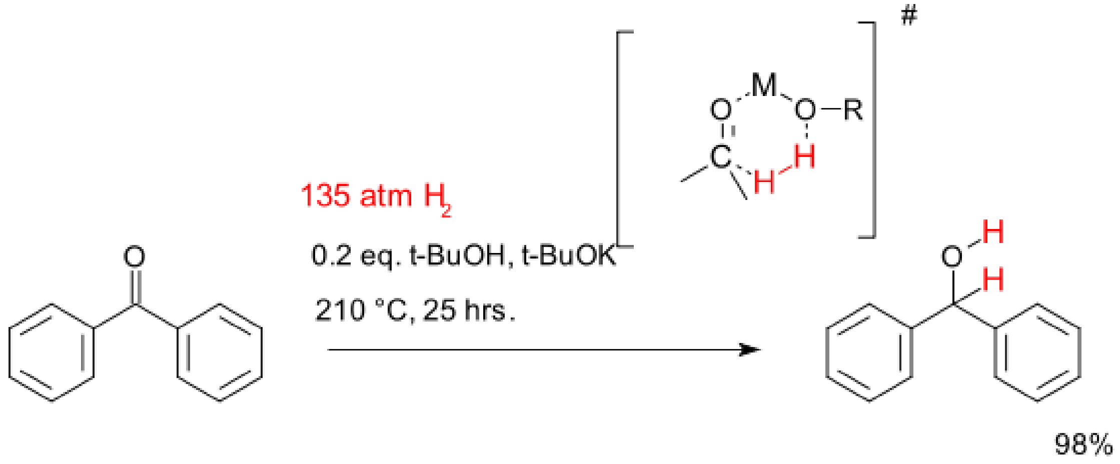
History

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.

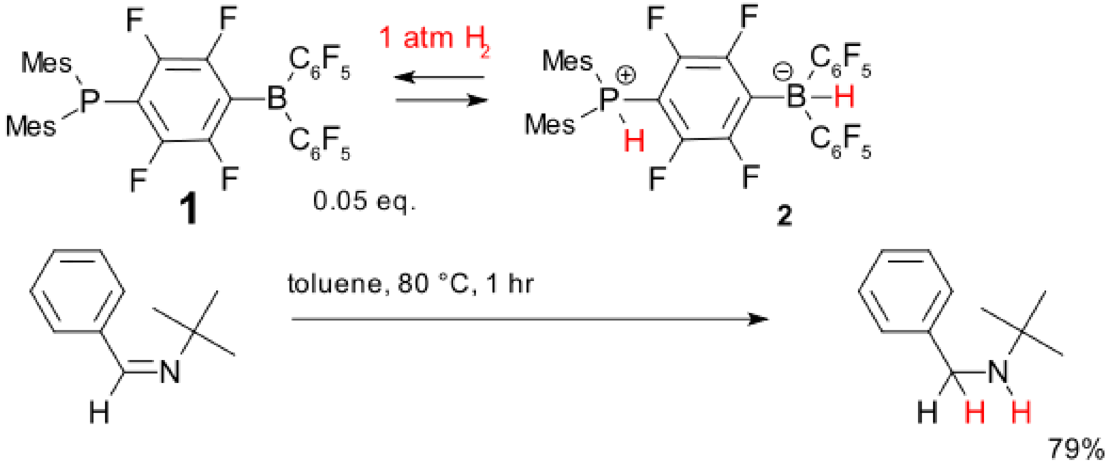
Metal-free hydrogenation

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

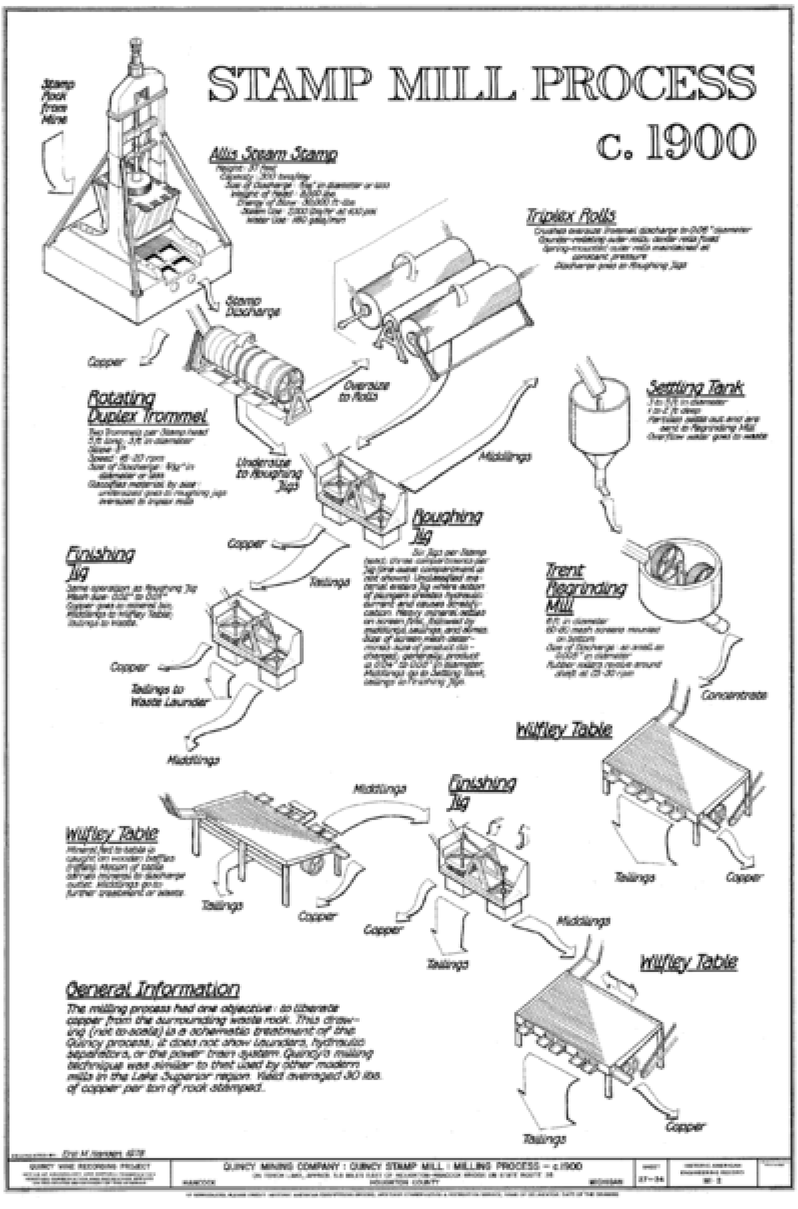
Flow hydrogenation has become a popular technique at the bench and increasingly the process scale. This technique involves continuously flowing a dilute stream of dissolved reactant over a fixed bed catalyst in the presence of hydrogen. Using established HPLC technology, this technique allows the application 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.

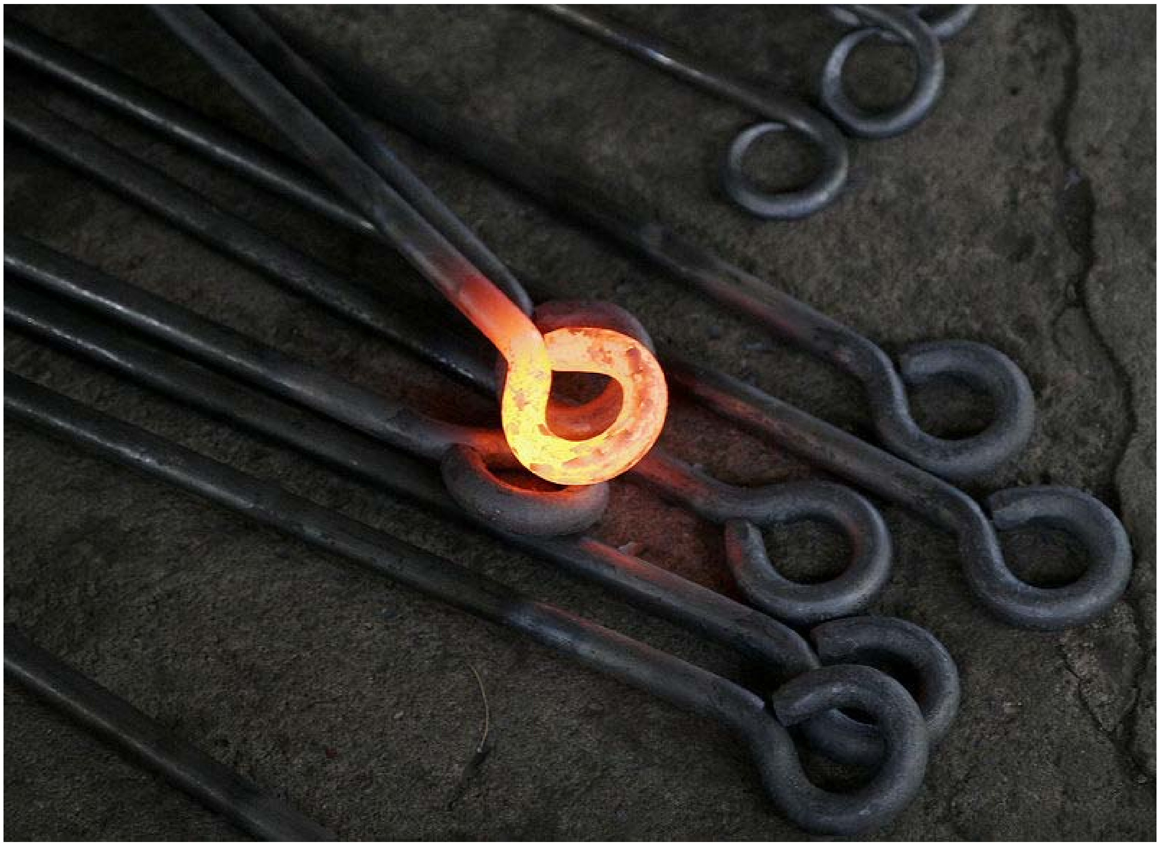
Convection

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.

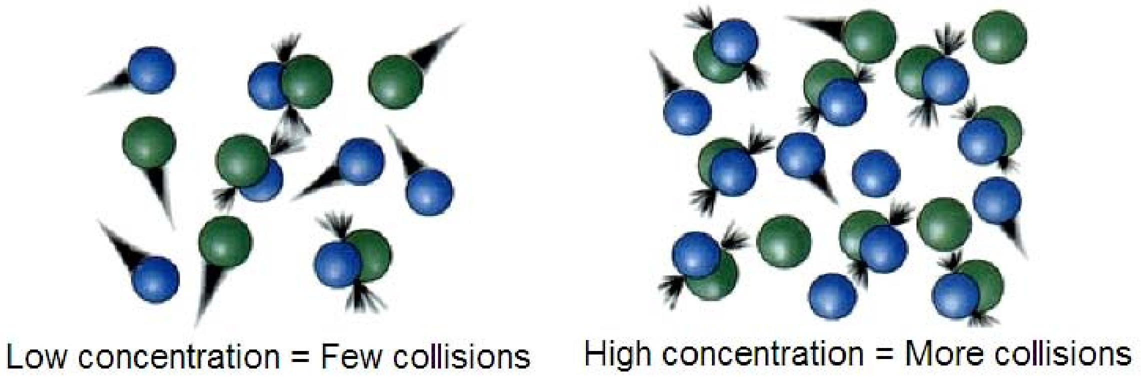
A thermocouple is a junction between two different metals that produces a voltage related to a temperature difference. Thermocouples are a widely used type of temperature sensor for measurement and control, and can also be used to convert heat into electric power.

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.

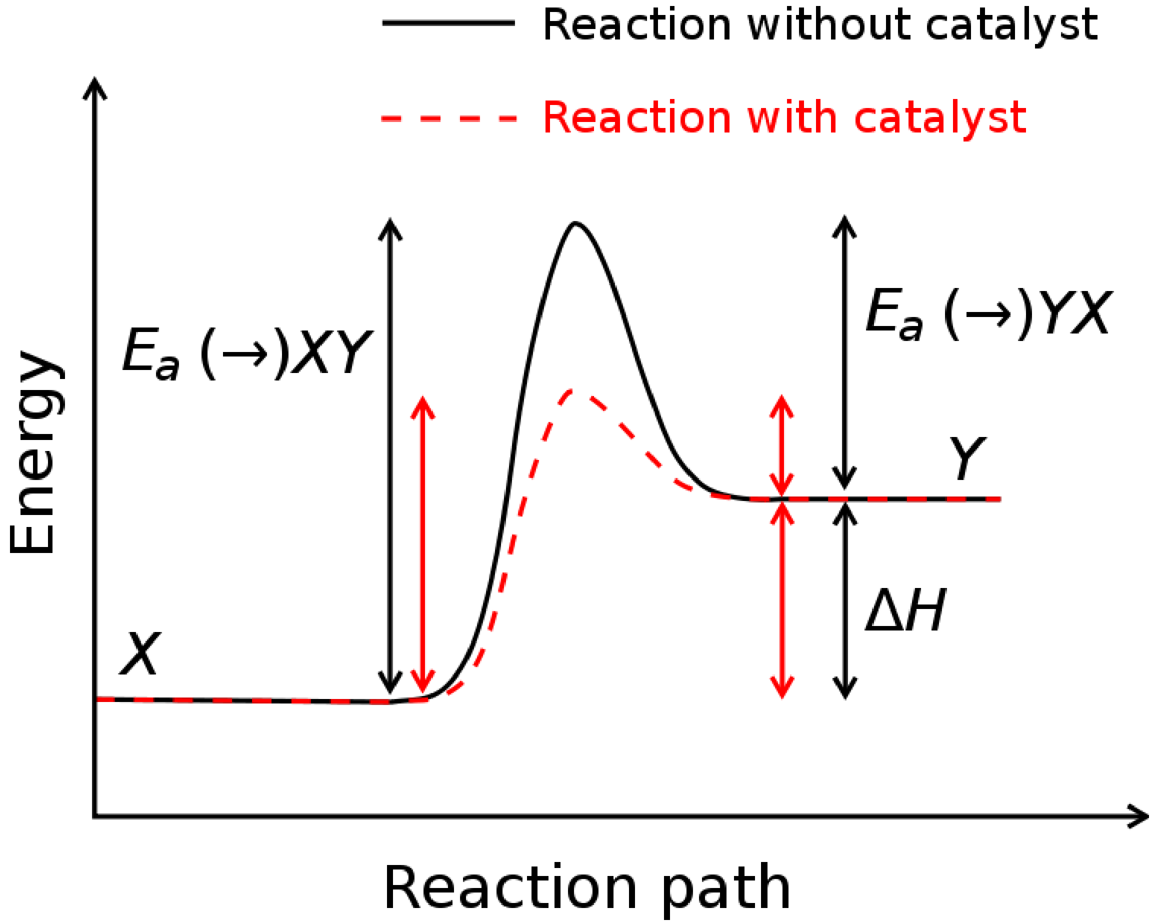
Temperature

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.

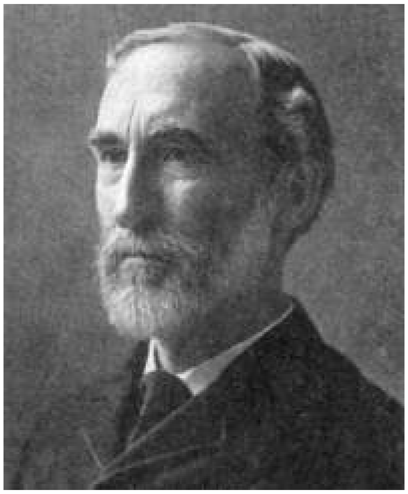
Chapter- 7

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

Another useful term is the heat of combustion, which is the energy released due to a combustion reaction and often applied in the study of fuels. Food is similar to hydrocarbon fuel and carbohydrate fuels, and when it is oxidized, its caloric content is similar (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* dξ_j/d*t*. 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 d*G* is now replace by an equality

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

or

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

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

Solutions

In solution chemistry and biochemistry, the Gibbs free energy decrease ($\partial G/\partial\xi$, in molar units, denoted cryptically by ΔG) is commonly used as a surrogate for (−*T* times) the entropy produced by spontaneous chemical reactions in situations where there is no work being done; or at least no "useful" work; i.e., other than perhaps some ± 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

Nuclear Reprocessing

Nuclear reprocessing uses chemical procedures to separate the useful components (especially the remaining uranium and the newly-created plutonium) from the fission products and other radioactive waste in spent nuclear fuel obtained from nuclear reactors. Reprocessing serves multiple purposes, whose relative importance has changed over time. Originally reprocessing was used solely to extract plutonium for producing nuclear weapons. With the commercialization of nuclear power, the reprocessed plutonium was recycled back into MOX nuclear fuel for thermal reactors. The reprocessed uranium, which constitutes the bulk of the spent fuel material, can in principle also be re-used as fuel, but that is only economic when uranium prices are high. Finally, the breeder reactor can employ not only the recycled plutonium and uranium in spent fuel, but all the actinides, closing the nuclear fuel cycle and potentially multiplying the energy extracted from natural uranium by more than 60 times. Nuclear reprocessing also reduces the volume of high-level nuclear waste and its radiotoxicity, allowing separate management (destruction or storage) of nuclear waste components.

Despite the energy and waste disposal benefits obtainable through nuclear reprocessing, reprocessing has been politically controversial because of the potential to contribute to nuclear proliferation, the potential vulnerability to nuclear terrorism, and because of its high cost compared to the once-through fuel cycle.

Separated components and disposition

The potentially useful components dealt with in nuclear reprocessing comprise specific actinides (plutonium, uranium, and some minor actinides). The lighter elements components include fission products, activation products, and cladding.

material	disposition
plutonium, minor actinides, reprocessed uranium	fission in fast, fusion, or subcritical reactor
reprocessed uranium, cladding, filters	less stringent storage as intermediate-level waste
long-lived fission and activation products	nuclear transmutation or geological repository

medium-lived fission products ^{137}Cs and ^{90}Sr	medium-term storage as high-level waste
useful radionuclides and noble metals	industrial and medical uses

History

The first large-scale nuclear reactors were built during World War II. These reactors were designed for the production of plutonium for use in nuclear weapons. The only reprocessing required, therefore, was the extraction of the plutonium (free of fission-product contamination) from the spent natural uranium fuel. In 1943, several methods were proposed for separating the relatively small quantity of plutonium from the uranium and fission products. The first method selected, a precipitation process called the Bismuth Phosphate process, was developed and tested at the Oak Ridge National Laboratory (ORNL) in the 1943-1945 period to produce quantities of plutonium for evaluation and use in weapons programs. ORNL produced the first macroscopic quantities (grams) of separated plutonium with these processes.

The Bismuth Phosphate process was first operated on a large scale at the Hanford Site, in the latter part of 1944. It was successful for plutonium separation in the emergency situation existing then, but it had a significant weakness: the inability to recover uranium.

The first successful solvent extraction process for the recovery of pure uranium and plutonium was developed at ORNL in 1949. The PUREX process is the current method of extraction. Separation plants were also constructed at Savannah River Site and a smaller plant at West Valley, New York which closed by 1972 because of its inability to meet new regulatory requirements.

Reprocessing of civilian fuel has long been employed in Europe, at the COGEMA La Hague site in France, the Sellafield site in the United Kingdom, the Mayak Chemical Combine in Russia, and at sites such as the Tokai plant in Japan, the Tarapur plant in India, and briefly at the West Valley Reprocessing Plant in the United States.

In October 1976, fear of nuclear weapons proliferation (especially after India demonstrated nuclear weapons capabilities using reprocessing technology) led President Gerald Ford to issue a Presidential directive to indefinitely suspend the commercial reprocessing and recycling of plutonium in the U.S. On April 7, 1977, President Jimmy Carter banned the reprocessing of commercial reactor spent nuclear fuel. The key issue driving this policy was the serious threat of nuclear weapons proliferation by diversion of plutonium from the civilian fuel cycle, and to encourage other nations to follow the USA lead. After that, only countries that already had large investments in reprocessing infrastructure continued to reprocess spent nuclear fuel. President Reagan lifted the ban in 1981, but did not provide the substantial subsidy that would have been necessary to start up commercial reprocessing.

In March 1999, the U.S. Department of Energy (DOE) reversed its own policy and signed a contract with a consortium of Duke Energy, COGEMA, and Stone & Webster (DCS) to design and operate a Mixed Oxide (MOX) fuel fabrication facility. Site preparation at the Savannah River Site (South Carolina) began in October 2005.

Separation technologies

Water and organic solvents

PUREX

PUREX, the current standard method, is an acronym standing for ***P**lutonium and **U**ranium **R**ecovery by **EX**traction*. The PUREX process is a liquid-liquid extraction method used to reprocess spent nuclear fuel, in order to extract uranium and plutonium, independent of each other, from the fission products. This is the most developed and widely used process in the industry at present. When used on fuel from commercial power reactors the plutonium extracted typically contains too much Pu-240 to be useful in a nuclear weapon. However, reactors that are capable of refuelling frequently can be used to produce weapon-grade plutonium, which can later be recovered using PUREX. Because of this, PUREX chemicals are monitored.

Modifications of PUREX

UREX

The PUREX process can be modified to make a **UREX** (**UR**anium **EX**traction) process which could be used to save space inside high level nuclear waste disposal sites, such as the Yucca Mountain nuclear waste repository, by removing the uranium which makes up the vast majority of the mass and volume of used fuel and recycling it as reprocessed uranium.

The UREX process is a PUREX process which has been modified to prevent the plutonium from being extracted. This can be done by adding a plutonium reductant before the first metal extraction step. In the UREX process, ~99.9% of the Uranium and >95% of Technetium are separated from each other and the other fission products and actinides. The key is the addition of acetohydroxamic acid (AHA) to the extraction and scrub sections of the process. The addition of AHA greatly diminishes the extractability of Plutonium and Neptunium, providing greater proliferation resistance than with the plutonium extraction stage of the PUREX process.

TRUEX

Adding a second extraction agent, octyl(phenyl)-N, N-dibutyl carbamoylmethyl phosphine oxide(CMPO) in combination with tributylphosphate, (TBP), the PUREX process can be turned into the **TRUEX** (**TR**ans**U**ranic **EX**traction) process. TRUEX was invented in the USA by Argonne National Laboratory and is designed to remove the transuranic metals (Am/Cm) from waste. The idea is that by lowering the alpha activity of the waste, the majority of the waste can then be disposed of with greater ease. In common with PUREX this process operates by a solvation mechanism.

DIAMEX

As an alternative to TRUEX, an extraction process using a malondiamide has been devised. The DIAMEX (**DIAM**ide**EX**traction) process has the advantage of avoiding the formation of organic waste which contains elements other than Carbon, Hydrogen, Nitrogen, and Oxygen. Such an organic waste can be burned without the formation of acidic gases which could contribute to acid rain. The DIAMEX process is being worked on in Europe by the French CEA. The process is sufficiently mature that an industrial plant could be constructed with the existing knowledge of the process. In common with PUREX this process operates by a solvation mechanism.

SANEX

Selective **A**cti**N**ide **EX**traction. As part of the management of minor actinides it has been proposed that the lanthanides and trivalent minor actinides should be removed from the PUREX raffinate by a process such as DIAMEX or TRUEX. In order to allow the actinides such as americium to be either reused in industrial sources or used as fuel, the lanthanides must be removed. The lanthanides have large neutron cross sections and hence they would poison a neutron driven nuclear reaction. To date the extraction system for the SANEX process has not been defined, but currently several different research groups are working towards a process. For instance the French CEA is working on a bis-triazinyl pyridine (BTP) based process. Other systems such as the dithiophosphinic acids are being worked on by some other workers.

UNEX

The ***UN**iversal* **EX**traction process was developed in Russia and the Czech Republic; it is designed to completely remove the most troublesome radioisotopes (Sr, Cs and minor actinides) from the raffinate remaining after the extraction of uranium and plutonium from used nuclear fuel. The chemistry is based upon the interaction of caesium and strontium with poly ethylene oxide (poly ethylene glycol) and a cobalt carborane anion (known as chlorinated cobalt dicarbollide). The actinides are extracted by CMPO, and the diluent is a polar aromatic such as nitrobenzene. Other dilents such as *meta*-nitrobenzotrifluoride and phenyl trifluoromethyl sulfone have been suggested as well.

Electrochemical methods

An exotic method using electrochemistry and ion exchange in ammonium carbonate has been reported.

Obsolete methods

Bismuth phosphate

The bismuth phosphate process is an obsolete process that adds significant unnecessary material to the final radioactive waste. The bismuth phospahate process has been replaced by solvent extraction processes. The bismuth phosphate process was designed to extract plutonium from aluminium-clad nuclear fuel rods, containing uranium. The fuel was declad by boiling it in caustic soda. After decladding, the uranium metal was dissolved in nitric acid.

The plutonium at this point is in the +4 oxidation state. It was then precipitated out of the solution by the addition of bismuth nitrate and phosphoric acid to form the bismuth phosphate. The plutonium was coprecipitated with this. The supernatant liquid (containing many of the fission products) was separated from the solid. The precipitate was then dissolved in nitric acid before the addition of an oxidant such as potassium permanganate which converted the plutonium to PuO_2^{2+} (Pu VI), then a dichromate salt was added to maintain the plutonium in the +6 oxidation state.

The bismuth phosphate was next re-precipitated leaving the plutonium in solution. Then an iron (II) salt such as ferrous sulfate was added, and the plutonium re-precipitated again using a bismuth phosphate carrier precipitate. Then lanthanum salts and fluoride were added to create solid lanthanum fluoride which acted as a carrier for the plutonium. This was converted to the oxide by the action of an alkali. The lanthanum plutonium oxide was next collected and extracted with nitric acid to form plutonium nitrate.

Hexone or Redox

This is a liquid-liquid extraction process which uses methyl isobutyl ketone as the extractant. The extraction is by a *solvation* mechanism. This process has the disadvantage of requiring the use of a salting-out reagent (aluminium nitrate) to increase the nitrate concentration in the aqueous phase to obtain a reasonable distribution ratio (D value). Also, hexone is degraded by concentrated nitric acid. This process has been replaced by the PUREX process.

$Pu^{4+} + 4NO_3^- + 2S \dashrightarrow [Pu(NO_3)_4S_2]$

Butex, β,β'-dibutyoxydiethyl ether

A process based on a solvation extraction process using the triether extractant named above. This process has the disadvantage of requiring the use of a salting-out reagent (aluminium nitrate) to increase the nitrate concentration in the aqueous phase to obtain a reasonable distribution ratio. This process was used at Windscale many years ago. This process has been replaced by PUREX.

Pyroprocessing

Pyroprocessing is a generic term for high-temperature methods. Solvents are molten salts (e.g. LiCl+KCl or LiF+CaF2) and molten metals (e.g. cadmium, bismuth, magnesium) rather than water and organic compounds. Electrorefining, distillation, and solvent-solvent extraction are common steps.

These processes are not currently in significant use worldwide, but they have been researched and developed at Argonne National Laboratory and elsewhere.

Advantages

- The principles behind them are well understood, and no significant technical barriers exist to their adoption.
- Readily applied to high-burnup spent fuel and requires little cooling time, since the operating temperatures are high already.
- Does not use solvents containing hydrogen and carbon, which are neutron moderators creating risk of criticality accidents and can absorb the fission product tritium and the activation product carbon-14 in dilute solutions that cannot be separated later.
    - Alternatively, voloxidation can remove 99% of the tritium from used fuel and recover it in the form of a strong solution suitable for use as a supply of tritium.
- More compact than aqueous methods, allowing on-site reprocessing at the reactor site, which avoids transportation of spent fuel and its security issues, instead storing a much smaller volume of fission products on site as high-level waste until decommissioning. For example, the Integral Fast Reactor and Molten Salt Reactor fuel cycles are based on on-site pyroprocessing.
- It can separate many or even all actinides at once and produce highly radioactive fuel which is harder to manipulate for theft or making nuclear weapons. (However, the difficulty has been questioned.) In contrast the PUREX process was designed to separate plutonium only for weapons, and it also leaves the minor actinides (americium and curium) behind, producing waste with more long-lived radioactivity.
- Most of the radioactivity in roughly 10^2 to 10^5 years after the use of the nuclear fuel is produced by the actinides, since there are no fission products with half-lives in this range. These actinides can fuel fast reactors, so extracting and reusing (fissioning) them reduces the long-term radioactivity of the wastes.

Disadvantages

- Reprocessing as a whole is not currently (2005) in favor, and places that do reprocess already have PUREX plants constructed. Consequently, there is little demand for new pyrometalurgical systems, although there could be if the Generation IV reactor programs become reality.

- The used salt from pyroprocessing is less suitable for conversion into glass than the waste materials produced by the PUREX process.

Electrolysis

PYRO-A and -B for IFR

These processes were developed by Argonne National Laboratory and used in the Integral Fast Reactor project.

PYRO-A is a means of separating actinides (elements within the actinide family, generally heavier than U-235) from non-actinides. The spent fuel is placed in an anode basket which is immersed in a molten salt electrolyte. An electrical current is applied, causing the uranium metal (or sometimes oxide, depending on the spent fuel) to plate out on a solid metal cathode while the other actinides (and the rare earths) can be absorbed into a liquid cadmium cathode. Many of the fission products (such as caesium, zirconium and strontium) remain in the salt. As alternatives to the molten cadmium electrode it is possible to use a molten bismuth cathode, or a solid aluminium cathode.

As an alternative to electrowinning, the wanted metal can be isolated by using a molten alloy of an electropositive metal and a less reactive metal.

Since the majority of the long term radioactivity, and volume, of spent fuel comes from actinides, removing the actinides produces waste that is more compact, and not nearly as dangerous over the long term. The radioactivity of this waste will then drop to the level of various naturally occurring minerals and ores within a few hundred, rather than thousands of, years.

The mixed actinides produced by pyrometallic processing can be used again as nuclear fuel, as they are virtually all either fissile, or fertile, though many of these materials would require a fast breeder reactor in order to be burned efficiently. In a thermal neutron spectrum, the concentrations of several heavy actinides (curium-242 and plutonium-240) can become quite high, creating fuel that is substantially different from the usual uranium or mixed uranium-plutonium oxides (MOX) that most current reactors were designed to use.

Another pyrochemical process, the **PYRO-B** process, has been developed for the processing and recycling of fuel from a transmuter reactor (a fast breeder reactor designed to convert transuranic nuclear waste into fission products). A typical transmuter fuel is free from uranium and contains recovered transuranics in an inert matrix such as metallic zirconium. In the PYRO-B processing of such fuel, an electrorefining step is used to separate the residual transuranic elements from the fission products and recycle the transuranics to the reactor for fissioning. Newly-generated technetium and iodine are extracted for incorporation into transmutation targets, and the other fission products are sent to waste.

Voloxidation

Voloxidation (for *volumetric oxidation*) involves heating oxide fuel with oxygen, sometimes with alternating oxidation and reduction, or alternating oxidation by ozone to uranium trioxide with decomposition by heating back to triuranium octoxide. A major purpose is to capture tritium as tritiated water vapor before further processing where it would be difficult to retain the tritium. Other volatile elements leave the fuel and must be recovered, especially iodine, technetium, and carbon-14. Voloxidation also breaks up the fuel or increases its surface area to enhance penetration of reagents in following reprocessing steps.

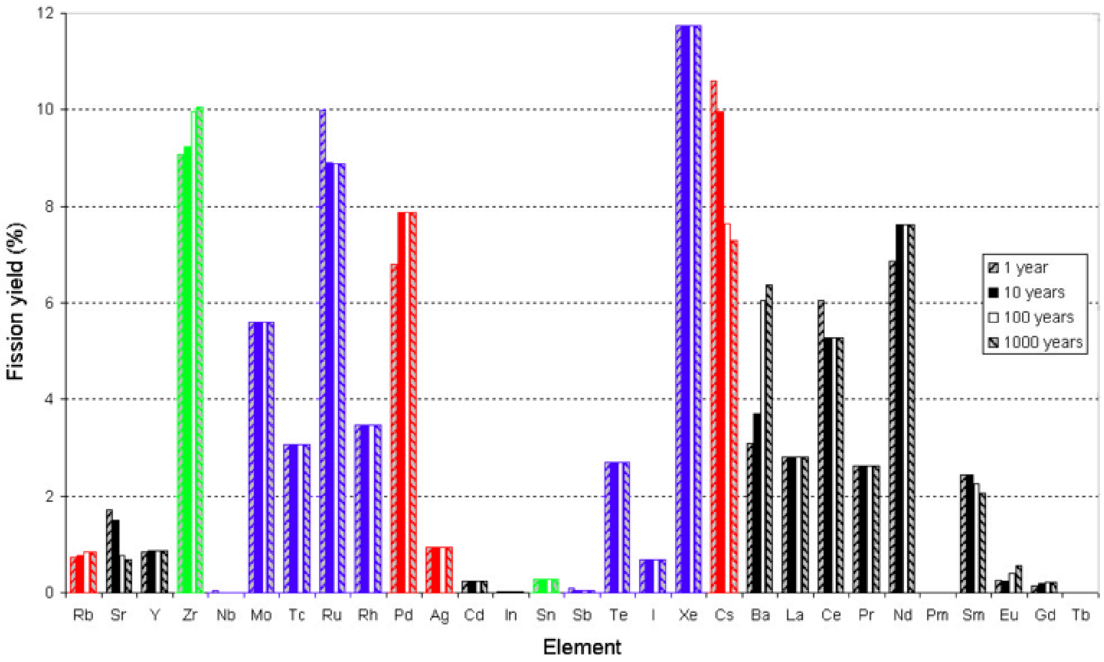
Volatilization in isolation

Simply heating spent oxide fuel in an inert atmosphere or vacuum at a temperature between 700°C and 1000°C as a first reprocessing step can remove several volatile elements, including caesium whose isotope cesium-137 emits about half of the heat produced by the spent fuel over the following 100 years of cooling (however, most of the other half is from strontium-90 which remains). The estimated overall mass balance for 20,000 grams of processed fuel with 2,000 grams of cladding is:

	Input	**Residue**	**Zeolite filter**	**Carbon filter**	**Particle filters**
Palladium	28	14	14		
Tellurium	10	5	5		
Molybdenum	70		70		
Caesium	46		46		
Rubidium	8		8		
Silver	2		2		
Iodine	4			4	
Cladding	2000	2000			
Uranium	19218	19218			?
Others	614	614			?
Total	22000	21851	145	4	0

Tritium is not mentioned in this paper.

Fluoride volatility



Blue elements have volatile fluorides or are already volatile; green elements do not but have volatile chlorides; red elements have neither, but the elements themselves or their oxides are volatile at very high temperatures. Yields at $10^{0,1,2,3}$ years after fission, not considering later neutron capture, fraction of 100% not 200%. Beta decay Kr-85→Rb, Sr-90→Zr, Ru-106→Pd, Sb-125→Te, Cs-137→Ba, Ce-144→Nd, Sm-151→Eu, Eu-155→Gd visible.

In the fluoride volatility process, fluorine is reacted with the fuel. Fluorine is so much more reactive than even oxygen that small particles of ground oxide fuel will burst into flame when dropped into a chamber full of fluorine. This is known as flame fluorination; the heat produced helps the reaction proceed. Most of the uranium, which makes up the bulk of the fuel, is converted to uranium hexafluoride, the form of uranium used in uranium enrichment, which has a very low boiling point. Technetium, the main long-lived fission product, is also efficiently converted to its volatile hexafluoride. A few other elements also form similarly volatile hexafluorides, pentafluorides, or heptafluorides. The volatile fluorides can be separated from excess fluorine by condensation, then separated from each other by fractional distillation or selective reduction. Uranium hexafluoride and technetium hexafluoride have very similar boiling points and vapor pressures, which makes complete separation more difficult.

Many of the fission products volatilized are the same ones volatilized in non-fluorinated, higher-temperature volatilization, such as iodine, tellurium and molybdenum; notable differences are that technetium is volatilized, but caesium is not.

Some transuranium elements such as plutonium, neptunium and americium can form volatile fluorides, but these compounds are not stable when the fluorine partial pressure is decreased. Most of the plutonium and some of the uranium will initially remain in ash which drops to the bottom of the flame fluorinator. The plutonium-uranium ratio in the ash may even approximate the composition needed for fast neutron reactor fuel. Further fluorination of the ash can remove all the uranium, neptunium, and plutonium as volatile fluorides; however, some other minor actinides may not form volatile fluorides and instead remain with the alkaline fission products. Some noble metals may not form fluorides at all, but remain in metallic form; however ruthenium hexafluoride is relatively stable and volatile.

Distillation of the residue at higher temperatures can separate lower-boiling transition metal fluorides and alkali metal (Cs, Rb) fluorides from higher-boiling lanthanide and alkaline earth metal (Sr, Ba) and yttrium fluorides. The temperatures involved are much higher, but can be lowered somewhat by distilling in a vacuum. If a carrier salt like lithium fluoride or sodium fluoride is being used as a solvent, high-temperature distillation is a way to separate the carrier salt for reuse.

Molten salt reactor designs carry out fluoride volatility reprocessing continuously or at frequent intervals. The goal is to return actinides to the molten fuel mixture for eventual fission, while removing fission products that are neutron poisons, or that can be more securely stored outside the reactor core while awaiting eventual transfer to permanent storage.

Chloride volatility and solubility

Many of the elements that form volatile high-valence fluorides will also form volatile high-valence chlorides. Chlorination and distillation is another possible method for separation. The sequence of separation may differ usefully from the sequence for fluorides; for example, zirconium tetrachloride and tin tetrachloride have relatively low boiling points of 331°C and 114.1°C. Chlorination has even been proposed as a method for removing zirconium fuel cladding, instead of mechanical decladding.

Chlorides are likely to be easier than fluorides to later convert back to other compounds, such as oxides.

Chlorides remaining after volatilization may also be separated by solubility in water. Chlorides of alkaline elements like americium, curium, lanthanides, strontium, caesium are more soluble than those of uranium, neptunium, plutonium, and zirconium.

Economics

The relative economics of reprocessing-waste disposal and interim storage-direct disposal has been the focus of much debate over the past ten years. Studies Template:Others? have modeled the total fuel cycle costs of a reprocessing-recycling system based on one-time recycling of plutonium in existing thermal reactors (as opposed to the proposed breeder reactor cycle) and compare this to the total costs of an open fuel cycle with direct disposal. The range of results produced by these studies is very wide, but all are agreed that under current (2005) economic conditions the reprocessing-recycle option is the more costly.

If reprocessing is undertaken only to reduce the radioactivity level of spent fuel it should be taken into account that spent nuclear fuel becomes less radioactive over time. After 40 years its radioactivity drops by 99.9%, though it still takes over a thousand years for the level of radioactivity to approach that of natural uranium. However the level of transuranic elements, including plutonium-239, remains high for over 100,000 years, so if not reused as nuclear fuel, then those elements need secure disposal because of nuclear proliferation reasons as well as radiation hazard.

Chapter- 9

Chemical Plant

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

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

Chemical processes

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

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

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

Continuous and batch operation

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

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

Units and fluid systems

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

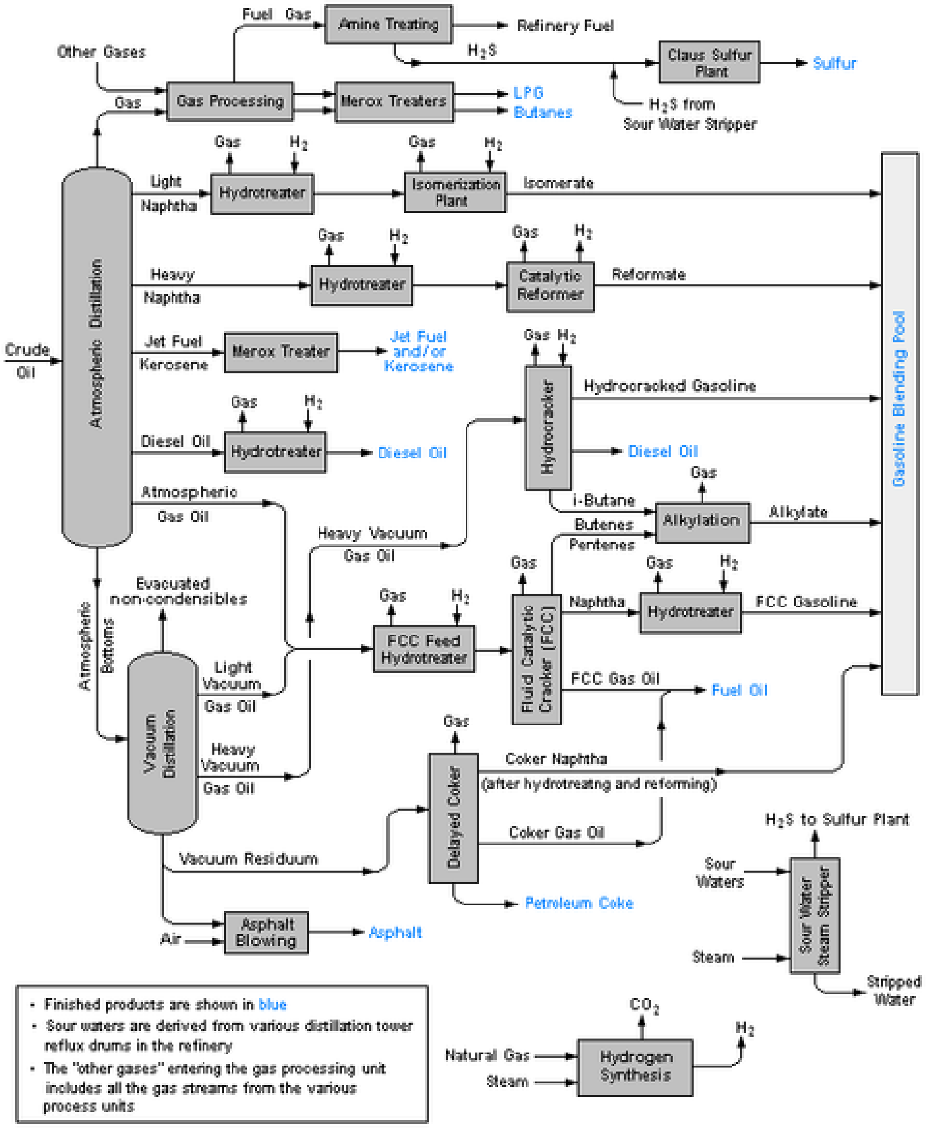
When designing plants on a large scale, heat produced or absorbed by chemical reactions should be considered. Some plants may have units with organism cultures for biochemical processes such as fermentation or enzyme production.

Distillation plant in Italy

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

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

Chemical plant design



Flow diagram for a typical oil refinery

The fundamental aspects of designing chemical plants are done by chemical engineers. In plant design, typically less than 1% of ideas for new designs ever become commercialized. During this solution process, typically, cost studies are used as an initial screening to eliminate unprofitable designs. If a process appears profitable, then other factors are considered, such as safety, environmental constraints, controllability, etc. The general goal in plant design, is to construct or synthesize “optimum designs” in the neighborhood of the desired constraints.

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

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

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

Units and fluid systems in the plant including all vessels, piping, tubing, valves, pumps, compressors, and other equipment must be rated or designed to be able to withstand the entire range of pressures, temperatures, and other conditions which they could possibly encounter, including any appropriate safety factors. All such units and equipment should also be checked for materials compatibility to ensure they can withstand long-term exposure to the chemicals they will come in contact with. Any closed system in a plant which has a means of pressurizing possibly beyond the rating of its equipment, such as heating, exothermic reactions, or certain pumps or compressors, should have an appropriately sized pressure relief valve included to prevent overpressurization for safety. Frequently all of these parameters (temperatures, pressures, flow, etc.) are exhaustively analyzed in combination through a *Hazop* or *fault tree analysis*, to ensure that the plant has no known risk of serious hazard.

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

Plant operation

Process control

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

Workers

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

Transport

Large quantities of fluid feedstock or product may enter or leave a plant by pipeline, railroad tank car, or tanker truck. For example, petroleum commonly comes to a refinery by pipeline. Pipelines can also carry petrochemical feedstock from a refinery to a nearby petrochemical plant. Natural gas is a product which comes all the way from a natural gas processing plant to final consumers by pipeline or tubing. Large quantities of liquid feedstock are typically pumped into process units. Smaller quantities of feedstock or product may be shipped to or from a plant in drums. Use of drums about 55 gallons in capacity is common for packaging industrial quantities of chemicals. Smaller batches of feedstock may be added from drums or other containers to process units by workers.

Maintenance

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

Statutory and regulatory compliance

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

Plant facilities

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

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

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

Corrosion and use of new materials

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