A

AAAS. The American Association for the Advancement of Science was founded in 1848 and incorporated in 1874. Its objectives are to further the work of scientists, to facilitate cooperation among them, to foster scientific freedom and responsibility, to improve the effectiveness of science in promoting human welfare, to advance education in science, and to increase public understanding and appreciation for the importance and promise of the methods of science in human progress. The AAAS head quarters is in Washington, DC. Additional information on the AAAS can be found at *http://www.aaas.org/* and *http://www.sciencemag.org/*.

ABACA. The sclerenchyma bundles from the sheathing leaf bases of *Musa textilis*, a plant closely resembling the edible banana plant. These bundles are stripped by hand, after which they are cleaned by drawing over a rough knife. The fiber bundles are now whitish and lustrous, and from six to twelve feet (1.8–3.6 meters) long. Being coarse, extremely strong and capable of resisting tension, they are much used in the manufacture of ropes and cables. Since the fibers swell only slightly when wet, they are particularly suited for rope that will be used in water. Waste manila fibers from rope manufacture and other sources are used in the making of a very tough grade of paper, known as manilla paper. The fibers may be obtained from both wild and cultivated plants, the latter yielding a product of better grade. The cultivated plants, propagated by seeds, by cuttings of the thick *rhizomes* or by suckers, are ready for harvest at the end of three years, after which a crop may be expected approximately every three years.

ABHERENT. Any substance that prevents adhesion of a material to itself or to another material. It may be in the form of a dry powder (a silicate such as talc, mica, or diatomaceous earth); a suspension (bentonite-water); a solution (soap-water); or a soft solid (stearic acid, tallow waxes). Abherents are used as dusting agents and mold washes in the adhesives, rubber, and plastics industries. Fats and oils are used as abherents in the baking industry. Fluorocarbon resin coatings on metals are widely used on cooking utensils.

ABLATING MATERIAL. A material, especially a coating material, designed to provide thermal protection to a body in a fluid stream through loss of mass. Ablating materials are used on the surfaces of some reentry vehicles to absorb heat by removal of mass, thus blocking the transfer of heat to the rest of the vehicle and maintaining temperatures within design limits. Ablating materials absorb heat by increasing in temperature and changing in chemical or physical state. The heat is carried away from the surface by a loss of mass (liquid or vapor). The departing mass also blocks part of the convective heat transfer to the remaining material in the same manner as transpiration cooling.

(1) Fibers made from white silica, fused in an oven, cut into blocks, and coated with borosilicate glass; these are extremely efficient at temperatures up to 2300F. (2) An all-carbon composite (called reinforced carbon-carbon) make by laminating and curing layers of graphite fiber previously coated with a resin, which is pyrolized to carbon. The resulting tile is then treated with a mixture of alumina, silicon, and silicon carbide. Such composites are used for maximum-temperature (nose cone) exposure up to 3000F. Both types are undamaged by the heat and are reusable. The tiles are adhered to the body of the spacecraft with a silicone adhesive. Ablative materials used on early spaceship trials were fluorocarbon polymers and glass-reinforced plastics, but these were wholly or partially decomposed during reentry.

ABLATION. The removal of surface material from a body by vaporization, melting, chipping, or other erosive process; specifically, the intentional removal of material from a nose cone or spacecraft during high-speed movement through a planetary atmosphere to provide thermal protection to the underlying structure. See also **Ablating Material**.

ABRASION. All metallic and nonmetallic surfaces, no matter how smooth, consist of minute serrations and ridges that induce a cutting or tearing action when two surfaces in contact move with respect to each other. This wearing of the surfaces is termed abrasion. Undesirable abrasion may occur in bearings and other machine elements, but abrasion is also adapted to surface finishing and machining, where the material is too hard to be cut by other means, or where precision is a primary requisite.

Temperature is a significant factor: friction may raise the temperature of the surface layers to the point where they become subject to chemical attack. Abrasion causes deterioration of many materials, especially of rubber (tire treads), where it can be offset by a high percentage of carbon black. Other materials subjected to abrasion in their service life are textiles (laundering), leather and plastics (shoe soles, belting), and house paints and automobile lacquers (airborne dust, grit, etc.).

See also **Abrasives**.

ABRASION pH. A term originated by Stevens and Carron in 1948 “to designate the pH values obtained by grinding minerals in water.” Abrasion pH measurements are useful in the field identification of minerals. The pH values range from 1 for ferric sulfate minerals, such as coquimbite, konelite, and rhomboclase, to 12 for calcium-sodium carbonates, such as gaylussite, pirssonite, and shortite. The recommended technique for determining abrasion pH is to grind, in a nonreactive mortar, a small amount of the mineral in a few drops of water for about one minute. Usually, a pH test paper is used. Values obtained in this manner are given in the middle column of Table 1. Another method, proposed by Keller et al. in 1963, involves the grinding of 10 grams of crushed mineral in 100 milliliters of water and noting the pH of the resulting slurry electronically. Values obtained in this manner are given in the right-hand column.

TABLE 1. ABRASION pH VALUES OF REPRESENTATIVE MINERALS

Mineral	pH by Stevens-Carron Method	pH by Keller et al. Method
Coquimbite	1	
Melanterite	2	
Alum	3	
Glauconite	5	5.5[a]
Kaolinite	5, 6, 7	5.5[a]
Anhydrite	6	
Barite	6	
Gypsum	6	
Quartz	6, 7	6.5
Muscovite	7, 8	8.0
Calcite	8	8.4
Biotite	8, 9	8.5
Microcline	8, 9	8.0 9.0[a]
Labradorite		8.0 9.2[a]
Albite	9, 10	
Dolomite	9, 10	8.5
Hornblende	10	8.9
Leucite	10	
Diopside	10, 11	9.9
Olivine	10, 11	9.6[a]
Magnesite	10, 11	

[a] More recent values published in literature.

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ABRASIVES. An abrasive is a substance used to abrade, smooth, or polish an object. If the object is soft, such as wood, then relatively soft abrasive materials may be used. Usually, however, abrasive connotes very hard substances ranging from naturally occurring sands to the hardest material known, diamond.

There are three basic forms of abrasives: grit (loose, granular, or powdered particles); bonded materials (particles are bonded into wheels, segments, or stick shapes); and coated materials (particles are bonded to paper, plastic, cloth, or metal).

Properties of Abrasive Materials

Hardness. Table 1 lists the various scales of hardness used for abrasives.

Toughness. An abrasive's toughness is often measured and expressed as the degree of friability, the ability of an abrasive grit to withstand impact without cracking, spalling, or shattering.

Refractoriness (Melting Temperature). Instantaneous grinding temperatures may exceed 3500°C at the interface between an abrasive and the workpiece being ground. Hence melting temperature is an important property.

Chemical Reactivity. Any chemical interaction between abrasive grains and the material being abraded affects the abrasion process.

Thermal Conductivity. Abrasive materials may transfer heat from the cutting tip of the grain to the bond posts, retaining the heat in a bonded wheel or coated belt. The cooler the cutting point, the harder it is.

Fracture. Fracture characteristics of abrasive materials are important, as well as the resulting grain shapes. Equiaxed grains are generally preferred for bonded abrasive products and sharp, acicular grains are preferred for coated ones. How the grains fracture in the grinding process determines the wear resistance and self-sharpening characteristics of the wheel or belt.

Microstructure. Crystal size, porosity, and impurity phases play a major role in fixing the fracture characteristics and toughness of an abrasive grain.

Natural Abrasives

Naturally occurring abrasives are still an important item of commerce, although synthetic abrasives now fill many of their former uses. They include diamonds, corundum, emery, garnet, silica, sandstone, tripoli, pumice, and pumicite.

Manufactured Abrasives

Manufactured abrasives include silicon carbide, fused aluminum oxide, sintered aluminum oxide, sol–gel sintered aluminum oxide, fused zirconia–alumina, synthetic diamond, cubic boron nitride, boron carbide, slags, steel shot, and grit.

Sizing, Shaping, and Testing of Abrasive Grains

Sizing. Manufactured abrasives are produced in a variety of sizes that range from a pea-sized grit of 4 (5.2 mm) to submicrometer diameters.

TABLE 1. SCALES OF HARDNESS

Material	Mohs' scale	Ridgeway's scale	Woodell's scale	Knoop hardness[a], kN/m^2[b]
talc	1			
calcite	3			
apatite	5			
vitreous silica		7		
topaz	8	9		13
corundum	9		9	20
fused ZrO_2/Al_2O_3[c]				16
SiC		13	14	24
cubic boron nitride				46
diamond	10	15	42.5	78

[a] At a 100-g load (K-100) average.

[b] To convert kN/m^2 to kgf/mm^2 divide by 0.00981.

[c] 39% ZrO_2 (NZ Alundum).

Shaping. Desired shapes are obtained by controlling the method of crushing and by impacting or mulling. In general, cubical particles are preferred for grinding wheels, whereas high aspect-ratio acicular particles are preferred for coated abrasive belts and disks.

Testing. Chemical analyses are done on all manufactured abrasives, as well as physical tests such as sieve analyses, specific gravity, impact strength, and loose poured density (a rough measure of particle shape). Special abrasives such as sintered sol–gel aluminas require more sophisticated tests such as electron microscope measurement of α-alumina crystal size, and indentation microhardness.

Coated Abrasives

Coated abrasives consist of a flexible backing on which films of adhesive hold a coating of abrasive grains. The backing may be paper, cloth, open-mesh cloth, vulcanized fiber (a specially treated cotton rag base paper), or any combination of these materials. The abrasives most generally used are fused aluminum oxide, sol–gel alumina, alumina–zirconia, silicon carbide, garnet, emery, and flint.

A new form of coated abrasive has been developed that consists of tiny aggregates of abrasive material in the form of hollow spheres. As these spheres break down in use, fresh cutting grains are exposed; this maintains cut-rate and keeps power low.

Bonded Abrasives

Grinding wheels are by far the most important bonded abrasive product both in production volume and utility. They are produced in grit sizes ranging from 4, for steel mill snagging wheels, to 1200, for polishing the surface of rotogravure rolls.

Marking System. Grinding wheels and other bonded abrasive products are specified by a standard marking system which is used throughout most of the world. This system allows the user to recognize the type of abrasive, the size and shaping of the abrasive grit, and the relative amount and type of bonding material.

Bond Type. Most bonded abrasive products are produced with either a vitreous (glass or ceramic) or a resinoid (usually phenolic resin) bond.

Special Forms of Bonded Abrasives. Special forms of bonded abrasives include honing and superfinishing stones, pulpstone wheels, crush-form grinding wheels, and creep feed wheels.

Superabrasive Wheels

Superabrasive wheels include diamond wheels and cubic boron nitride (CBN) wheels.

Grinding Fluids

Grinding fluids or coolants are fluids employed in grinding to cool the work being ground, to act as a lubricant, and to act as a grinding aid. Soluble oil coolants in which petroleum oils are emulsified in water have been developed to impart some lubricity along with rust-preventive properties.

Loose Abrasives

In addition to their use in bonded and coated products, both natural and manufactured abrasive grains are used loose in such operations as polishing, buffing, lapping, pressure blasting, and barrel finishing.

Jet Cutting

High pressure jet cutting with abrasive grit can be used on metals to produce burn-free cuts with no thermal or mechanical distortion.

Health and Safety

Except for silica and natural abrasives containing free silica, the abrasive materials used today are classified by NIOSH as nuisance dust materials and have relatively high permissible dust levels.

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ABSOLUTE 1. Pertaining to a measurement relative to a universal constant or natural datum, as absolute coordinate system, absolute altitude, absolute temperature. See also **Absolute Temperature**. 2. Complete, as in absolute vacuum.

ABSOLUTE TEMPERATURE. The fundamental temperature scale used in theoretical physics and chemistry, and in certain engineering calculations such as the change in volume of a gas with temperature. Absolute temperatures are expressed either in degrees Kelvin or in degrees Rankine, corresponding respectively to the centigrade and Fahrenheit scales. Temperatures in Kelvins are obtained by adding 273 to the centigrade temperature (if above °C) or subtracting the centigrade temperature from 273 (if below °C). Degrees Rankine are obtained by subtracting 460 from the Fahrenheit temperature.

ABSOLUTE ZERO. Conceptually that temperature where there is no molecular motion, no heat. On the Celsius scale, absolute zero is −273.15°C, on the Fahrenheit scale, −459.67°F; and zero Kelvin (0 K). The concept of absolute zero stems from thermodynamic postulations.

Heat and temperature were poorly understood prior to Carnot's analysis of heat engines in 1824. The Carnot cycle became the conceptual foundation for the definition of temperature. This led to the somewhat later work of Lord Kelvin, who proposed the Kelvin scale based upon a consideration of the second law of thermodynamics. This leads to a temperature at which all the thermal motion of the atoms stops. By using this as the zero point or absolute zero and another reference point to determine the size of the degrees, a scale can be defined. The Comit'e Consultative of the International Committee of Weights and Measures selected 273.16 K as the value for the triple point for water. This set the ice-point at 273.15 K.

From the standpoint of thermodynamics, the thermal efficiency E of an engine is equal to the work W derived from the engine divided by the heat supplied to the engine, $Q2$. If $Q1$ is the heat exhausted from the engine,

$$E = (W/Q2) = (Q2 - Q1)/Q2 = 1 - (Q1/Q2)$$

where W, $Q1$, and $Q2$ are all in the same units. A Carnot engine is a theoretical one in which all the heat is supplied at a single high temperature and the heat output is rejected at a single temperature. The cycle consists of two adiabatics and two isothermals. Here the ratio $Q1/Q2$ must depend only on the two temperatures and on nothing else. The Kelvin temperatures are then defined by the relation where $Q1/Q2$ is the ratio of the heats rejected and absorbed, and $T1/T2$ is the ratio of the Kelvin temperatures of the reservoir and the source. If one starts with a given size for the degree, then the equation completely defines a thermodynamic temperature scale.

$$\frac{Q1}{Q2} = \frac{T1}{T2}$$

A series of Carnot engines can be postulated so that the first engine absorbs heat Q from a source, does work W, and rejects a smaller amount of heat at a lower temperature. The second engine absorbs all the heat rejected by the first one, does work, and rejects a still smaller amount of heat which is absorbed by a third engine, and so on. The temperature at which each successive engine rejects its heat becomes smaller and smaller, and in the limit this becomes zero so that an engine is reached which rejects no heat at a temperature that is absolute zero. A reservoir at absolute zero cannot have heat rejected to it by a Carnot engine operating between a higher temperature reservoir and the one at absolute zero. This can be used as the definition of absolute zero. Absolute zero is then such a temperature that a reservoir at that temperature cannot have heat rejected to it by a Carnot engine which uses a heat source at some higher temperature.

ABSORPTIMETRY. A method of instrumental analysis, frequently chemical, in which the absorption (or absence thereof) of selected electromagnetic radiation is a qualitative (and often quantitative) indication of the chemical composition of other characteristics of the material under observation. The type of radiation utilized in various absorption-type instruments ranges from radio and microwaves through infrared, visible, and ultraviolet radiation to x-rays and gamma rays. See also **Analysis (Chemical)**; and **Spectro Instruments**.

ABSORPTION BAND. A range of wavelengths (or frequencies) in the electromagnetic spectrum within which radiant energy is absorbed by a substance. When the absorbing substance is a polyatomic gas, an absorption band actually is composed of a group of discrete absorption lines, which appear to overlap. Each line is associated with a particular mode of vibration or rotation induced in a gas molecule by the incident radiation. The absorption bands of oxygen and ozone are often referred to in the literature of atmospheric physics.

The important bands for oxygen are (1) the Hopfield bands, very strong, between about 670 and 1000 angstroms in the ultraviolet; (2) a diffuse system between 1019 and 1300 angstroms; (3) the Schumann-Runge continuum, very strong, between 1350 and 1760 angstroms; (4) the Schumann-Runge bands between 1760 and 1926 angstroms; (5) the Herzberg bands between 2400 and 2600 angstroms; (6) the atmospheric bands between 5380 and 7710 angstroms in the visible spectrum; and (7) a system in the infrared at about 1 micron.

The important bands for ozone are the Hartley bands between 2000 and 3000 angstroms in the ultraviolet, with a very intense maximum absorption at 2550 angstroms; the Huggins bands, weak absorption between 3200 and 3600 angstroms; the Chappius bands, a weak diffuse system between 4500 and 6500 angstroms in the visible spectrum; and the infrared bands centered at 4.7, 9.6 and 14.1 microns, the latter being the most intense.

See also **Absorption Spectrum**; and **Electromagnetic Spectrum**.

ABSORPTION COEFFICIENT 1. For the absorption of one substance or phase in another, as in the absorption of a gas in a liquid, the absorption coefficient is the volume of gas dissolved by a specified volume of solvent; thus a widely used coefficient is the quantity a in the expression $\alpha = V_0/V_p$, where V_0 is the volume of gas reduced to standard conditions, V is the volume of liquid, and p is the partial pressure of the gas.

2. In the case of sound, the absorption coefficient (which is also called the acoustical absorptivity) is defined as the fraction of the incident sound energy absorbed by a surface or medium, the surface being considered part of an infinite area.

3. In the most general use of the term, absorption coefficient, applied to electromagnetic radiation and atomic and subatomic particles, is a measure of the rate of decrease in intensity of a beam of photons or particles in its passage through a particular substance. One complication in the statement of the absorption coefficient arises from the cause of the decrease in intensity. When light, x-rays, or other electromagnetic radiation enters a body of matter, it experiences in general two types of attenuation. Part of it is subjected to scattering, being reflected in all directions, while another portion is absorbed by being converted into other forms of energy. The scattered radiation may still be effective in the same ways as the original, but the absorbed portion ceases to exist as radiation or is re-emitted as secondary radiation. Strictly, therefore, we have to distinguish the true absorption coefficient from the scattering coefficient; but for practical purposes it is sometimes convenient to add them together as the total attenuation or extinction coefficient.

If appropriate corrections are made for scattering and related effects, the ratio I/I_0 is given by the laws of Bouguer and Beer. Here, I_0 is the intensity or radiant power of the light incident on the sample and I is the intensity of the transmitted light. This ratio $I/I_0 = T$ is known as the transmittance. See also **Spectrochemical Analysis (Visible)**.

ABSORPTION (Process). Absorption is commonly used in the process industries for separating materials, notably a specific gas from a mixture of gases; and in the production of solutions such as hydrochloric and sulfuric acids. Absorption operations are very important to many air pollution abatement systems where it is desired to remove a noxious gas, such as sulfur dioxide or hydrogen sulfide, from an effluent gas prior to releasing the material to the atmosphere. The absorption medium is a liquid in which (1) the gas to be removed, i.e., absorbed is soluble in the liquid, or (2) a chemical reaction takes place between the gas and the absorbing liquid. In some instances a chemical reagent is added to the absorbing liquid to increase the ability of the solvent to absorb.

Wherever possible, it is desired to select an absorbing liquid that can be regenerated and thus recycled and used over and over. An example of absorption with chemical reaction is the absorption of carbon dioxide from a flue gas with aqueous sodium hydroxide. In this reaction, sodium carbonate is formed. This reaction is irreversible. However, continued absorption of the carbon dioxide with the sodium carbonate solution results in the formation of sodium acid carbonate. The latter can be decomposed upon heating to carbon dioxide, water, and sodium carbonate and thus the sodium carbonate can be recycled.

Types of equipment used for absorption include (1) a packed tower filled with packing material, absorbent liquid flowing down through the packing (designed to provide a maximum of contact surface), and gas flowing upward in a countercurrent fashion; (2) a spray tower in which the absorbing liquid is sprayed into essentially an empty tower with the gas flowing upward; (3) a tray tower containing bubble caps, sieve trays, or valve trays; (4) a falling-film absorber or wetted-wall column; and (5) stirred vessels. Packed towers are the most commonly used.

A representative packed-type absorption tower is shown in Fig. 1. In addition to absorption efficiency, a primary concern of the tower designer is that of minimizing the pressure drop through the tower. The principal elements of pressure drop are shown at the right of the diagram. Important to efficiency of absorption and pressure drop is the type of packing used. As shown by Fig. 2, over the years numerous types of packing (mostly ceramic) have been developed to meet a wide variety of operating parameters. A major objective is that of providing as much contact surface as is possible with a minimum of pressure drop. Where corrosion conditions permit, metal packing sometimes can be used. Of the packing designs illustrated, the berl saddles range in size from ovrtextstyle1over4 inch (6 millimeters) up to 2 inches (5 centimeters); raschig rings range from ovrtextstyle1over4 inch (6 millimeters) up to 4 inches (10 centimeters); lessing rings range from 1 inch (2.5 centimeters) up to 2 inches (5 centimeters); partition and spiral rings range from 3 inches (7.5 centimeters) up to 6 inches (15 centimeters).

In operation, the absorbing liquid is pumped into the top of the column where it is distributed by means of a weir to provide uniform distribution of the liquid over the underlying packing. Gas enters at the base of the tower and flows upward (countercurrent with the liquid) and out the top of the tower. The liquid may or may not be recycled without regeneration, depending upon the strength of the absorbent versus the quantity of material (concentration) in the gas to be removed. In a continuous operation, of course, a point is reached where fresh absorbing liquid must be added.

It is interesting to note that over 100,000 of the $\frac{1}{4}$-inch (6-millimeter) size packing shapes will be contained in each cubic foot (0.02832 cubic meter) of tower space if dense packing is desired.

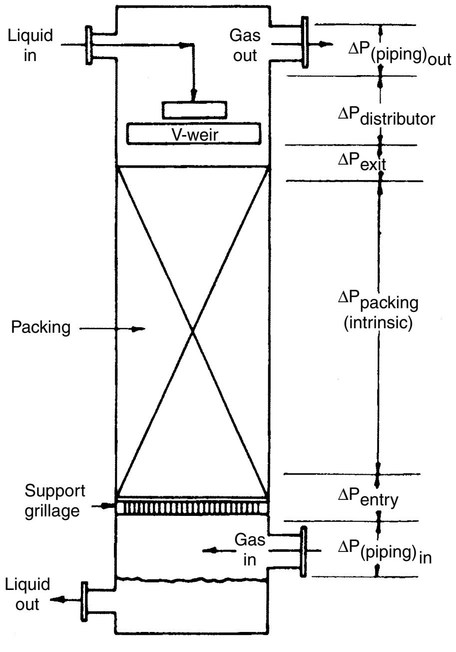

Fig. 1. Section of representative packed absorption tower

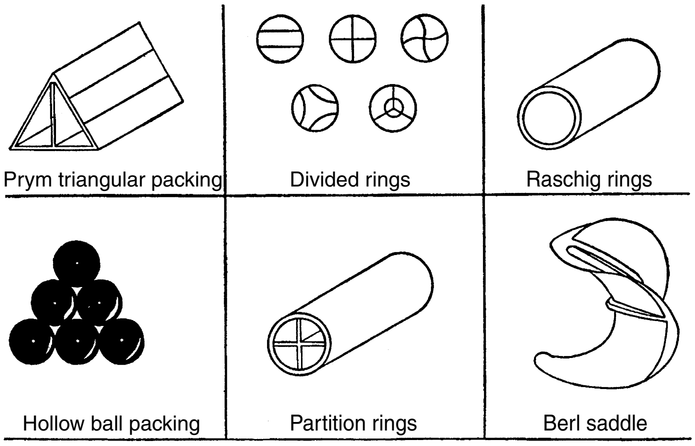

Fig. 2. Types of packing used in absorption towers

In the purification of natural gas, the gas is fed into the bottom of an absorption tower where the gas is contacted countercurrently by a lean absorption oil. Hydrochloric acid is produced by absorbing gaseous hydrogen chloride in water, usually in a spray-type tower. Unreacted ammonia in the manufacture of hydrogen cyanide is absorbed in dilute sulfuric acid. In the production of nitric acid, ammonia is catalytically oxidized and the gaseous products are absorbed in water. The ethanolamines are widely used in scrubbing gases for removal of acid compounds. Hydrocarbon gases containing hydrogen sulfide can be scrubbed with monoethanolamine, which combines with it by salt formation and effectively removes it from the gas stream. In plants synthesizing ammonia, hydrogen and carbon dioxide are formed. The hydrogen can be obtained by countercurrently scrubbing the gas mixture in a packed or tray column with monoethanolamine which absorbs the carbon dioxide. The latter can be recovered by heating the monoethanolamine. In a nonliquid system, sulfur dioxide can be absorbed by dry cupric oxide on activated alumina, thus avoiding the disadvantages of a wet process. Sulfuric acid is produced by absorbing sulfur trioxide in weak acid or water.

See also **Coal**; **Ethanolamines**; **Chromatography**; and **Pollution (Air)**.

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ABSORPTION SPECTROSCOPY. An important technique of instrumental analysis involving measurement of the absorption of radiant energy by a substance as a function of the energy incident upon it. Adsorption processes occur throughout the electromagnetic spectrum, ranging from the γ region (nuclear resonance absorption of the Mossbauer effect) to the radio region (nuclear magnetic resonance). In practice, they are limited to those processes that are followed by the emission of radiant energy of greater intensity than that which was absorbed. All absorption process involve absorption of a photon by the substance being analyzed. If it loses the excess energy by emitting a photon of less energy than that absorbed, fluorescence or phosphorescence is said to occur, depending on the lifetime of the excited state.

The emitted energy is normally studied. If the source of radiant energy and the absorbing species are in identical energy states (in resonance), the excess energy is often given up by the nondirectional emission of a photon whose energy is identical with the absorbed.

Either adsorption or emission may be studied, depending upon the chemical and instrumental circumstances. If the emitted energy is studied, the term *resonance fluorescence* is often used. However, if the absorbing species releases the excess energy in small steps by intermolecular collision or some other process, it is commonly understood that this phenomenon falls within the realm of absorption spectroscopy. The terms *absorption spectroscopy, spectrophotometry*, and *absorptimetry* are often used synonymously.

Most absorption spectroscopy is done in the ultraviolet, visible, and infrared regions of the electromagnetic spectrum.

See also **Emission Spectroscopy**; and **Infrared Radiation**.

ABSORPTION SPECTRUM. The spectrum of radiation that has been filtered through a material medium. When white light traverses a transparent medium, a certain portion of it is absorbed, the amount varying, in general, progressively with the frequency of which the absorption coefficient is a function. Analysis of the transmitted light may, however, reveal that certain frequency ranges are absorbed to a degree out of all proportion to the adjacent regions; that is, with a distinct selectivity. These abnormally absorbed frequencies constitute, collectively, the "absorption spectrum" of the medium, and appear as dark lines or bands in the otherwise continuous spectrum of the transmitted light. The phenomenon is not confined to the visible range, but may be found to extend throughout the spectrum from the far infrared to the extreme ultraviolet and into the x-ray region.

A study of such spectra shows that the lines or bands therein accurately coincide in frequency with certain lines or bands of the emission spectra of the same substances. This was formerly attributed to resonance of electronic vibrations, but is now more satisfactorily explained by quantum theory on the assumption that those quanta of the incident radiation which are absorbed are able to excite atoms or molecules of the medium to some (but not all) of the energy levels involved in the production of the complete emission spectrum.

A very familiar example is the spectrum of sunlight, which is crossed by innumerable dark lines, the Fraunhofer lines, much has been learned about the constitution of the sun, stars, and other astronomical objects from the Fraunhofer lines.

A noteworthy characteristic of selective absorption is found in the existence of certain anomalies in the refractive index in the neighborhood of absorption frequencies; discussed under Dispersion. See also **Absorption Band**; and **Electromagnetic Spectrum**.

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ABS RESINS (Acrylonitrile-Butadiene-Styrene). See **Resins (Acrylonitrile-Butadiene-Styrene)**.

ABUNDANCE. The relative amount (% by weight) of a substance in the earth's crust, including the atmosphere and the oceans.

(1) The abundance of the elements in the earth's crust is shown in Table 1.

(2) The percentages of inorganic compounds in the earth's crust, exclusive of water, are:

(1) SiO_2	55	(2) Al_2O_3	15	(3) $CaCO_3$	8.8
(4) MgO	1.6	(5) Na_2O	1.6	(6) K_2O	1.9

TABLE 1.

Rank	Element	% by wt.
1	Oxygen	49.2
2	Silicon	25.7
3	Aluminum	7.5
4	Iron	4.7
5	Calcium	3.4
6	Sodium	2.6
7	Potassium	2.4
8	Magnesium	1.9
9	Hydrogen	0.9
10	Titanium	0.6
11	Chlorine	0.2
12	Phosphorus	0.1
13	Manganese	0.1
14	Carbon	0.09
15	Sulfur	0.05
16	Barium	0.05
	all others	0.51

(3) The most abundant organic materials are cellulose and its derivatives, and proteins.

Note: In the universe as a whole, the most abundant element is hydrogen.

ACARICIDE. A substance, natural or synthetic, used to destroy or control infestations of the animals making up *Arachnida, Acarina*, mainly mites and ticks, some forms of which are very injurious to both plants and livestock, including poultry. There are numerous substances that are effective both as acaricides and insecticides; others of a narrower spectrum are strictly acaricides. See also **Insecticide**; and **Insecticide and Pesticide Technology**.

ACCELERATOR 1. A compound, usually organic, that greatly reduces the time required for vulcanization of natural and synthetic rubbers, at the same time improving the aging and other physical properties. See also **Rubber (Natural)**. Organic accelerators invariably contain nitrogen, and many also contain sulfur. The latter type are called *ultra-accelerators* because of their greater activity. The major types include amines, guanidines, thiazoles, thiuram sulfides, and dithiocarbamates. The amines and guanidines are basic, the others acidic. The normal effective concentration of organic accelerators in a rubber mixture is 1% or less depending on the rubber hydrocarbon present. Zinc oxide is required for activation, and in the case of acidic accelerators, stearic acid is required. The introduction of organic accelerators in the early twenties was largely responsible for the successful development of automobile tires and mechanical products for engineering uses. A few inorganic accelerators are still used in low-grade products, e.g., lime, magnesium oxide, and lead oxide.

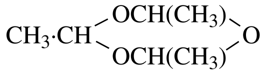
2. A compound added to a photographic developer to increase its activity, such as certain quaternary ammonium compounds and alkaline substances.

3. A particle accelerator.

ACETALDEHYDE. [CAS: 75-07-0]. CH_3CHO, formula weight 44.05, colorless, odorous liquid, mp −123.5°C, bp 20.2°C, sp gr 0.783. Also known as *ethanal*, acetaldehyde is miscible with H_2O, alcohol, or ether in all proportions. Because of its versatile chemical reactivity, acetaldehyde is widely used as a commencing material in organic syntheses, including the production of resins, dyestuffs, and explosives. The compound also is used as a reducing agent, preservative, and as a medium for silvering mirrors. In resin manufacture, paraldehyde $(CH_3CHO)_3$ sometimes is preferred because of its higher boiling and flash points.

In tonnage production, acetaldehyde may be manufactured by (1) the direct oxidation of ethylene, requiring a catalytic solution of copper chloride plus small quantities of palladium chloride, (2) the oxidation of ethyl alcohol with sodium dichromate, and (3) the dry distillation of calcium acetate with calcium formate.

Acetaldehyde reacts with many chemicals in a marked manner, (1) with ammonio-silver nitrate ("Tollen's solution"), to form metallic silver, either as a black precipitate or as an adherent mirror film on glass, (2) with alkaline cupric solution ("Fehling's solution") to form cuprous oxide, red to yellow precipitate, (3) with rosaniline (fuchsine, magenta), which has been decolorized by sulfurous acid ("Schiff's solution"), the pink color of rosaniline is restored, (4) with NaOH, upon warming, a yellow to brown resin of unpleasant odor separates (this reaction is given by aldehydes immediately following acetaldehyde in the series, but not by formaldehyde, furfuraldehyde or benzaldehyde), (5) with anhydrous ammonia, to form aldehyde-ammonia $CH_3\cdot CHOH\cdot NH_2$, white solid, mp 97°C, bp 111°C, with decomposition, (6) with concentrated H_2SO_4, heat is evolved, and with rise of temperature, paraldehyde $(C_2H_4O)_3$ or



$$CH_3{\cdot}CH\begin{matrix}\diagup OCH(CH_3)\diagdown \\ \diagdown OCH(CH_3)\diagup\end{matrix}O$$

colorless liquid bp 124°C, slightly soluble in H_2O, is formed, (7) with acids, below 0°C, forms metaldehyde $(C_2H_4O)x$, white solid, sublimes at about 115°C without melting but with partial conversion to acetaldehyde, (8) with dilute HCl or dilute NaOH, aldol, $CH_3\cdot CHOH\cdot CH_2CHO$ slowly forms, (9) with phosphorus pentachloride, forms ethylidene chloride, $CH_3\cdot CHCl_2$, colorless liquid, bp 58°C, (10) with ethyl alcohol and dry hydrogen chloride, forms acetal, 1,1-diethyoxyethane $CH_3\cdot CH(OC_2H_5)_2$, colorless liquid, bp 104°C, (11) with hydrocyanic acid, forms acetaldehyde cyanohydrin, $CH_3\cdot CHOH\cdot CN$, readily converted into alphahydroxypropionic acid, $CH_3\cdot CHOH\cdot COOH$, (12) with sodium hydrogen sulfite, forms acetaldehyde sodium bisulfite, $CH_3\cdot CHOH\cdot SO_3Na$, white solid, from which acetaldehyde is readily recoverable by treatment with sodium carbonate solution, (13) with hydroxylamine hydrochloride forms acetaldoxime, $CH_3\cdot CH{:}NOH$, white solid, mp 47°C, (14) with phenylhydrazine, forms acetaldehyde phenylhydrazone, $CH_3\cdot CH{:}N\cdot NH\cdot C_6H_5$, white solid, mp 98°C, (15) with magnesium methyl iodide in anhydrous ether ("Grignard's solution"), yields, after reaction with water, isopropyl alcohol, $(CH_3)_2CHOH$, a secondary alcohol, (16) with semicarbazide, forms acetaldehyde semicarbazone, $CH_3\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2$, white solid, mp 162°C, (17) with chlorine, forms trichloroacetaldehyde ("chloral"), $CCl_3\cdot CHO$, (18) with H_2S, forms thioacetaldehyde, $CH_3\cdot CHS$ or $(CH_3\cdot CHS)_3$. Acetaldehyde stands chemically between ethyl alcohol on one hand—to which it can be reduced—and acetic acid on the other hand—to which it can be oxidized. These reactions of acetaldehyde, coupled with its ready formation from acetylene by mercuric sulfate solution as a catalyzer, open up a vast field of organic chemistry with acetaldehyde as raw material: acetaldehyde hydrogenated to ethyl alcohol; oxygenated to acetic acid, thence to acetone, acetic anhydride, vinyl acetate, vinyl alcohol. Acetaldehyde is also formed by the regulated oxidation of ethyl alcohol by such a reagent as sodium dichromate in H_2SO_4 (chromic sulfate also produced). Reactions (1), (3), (14), and (16) above are most commonly used in the detection of acetaldehyde. See also **Aldehydes**.

ACETAL GROUP. An organic compound of the general formula $RCH(OR')(OR'')$ is termed an *acetal* and is formed by the reaction of an aldehyde with an alcohol, usually in the presence of small amounts of acids or appropriate inorganic salts. Acetals are stable toward alkali, are volatile, insoluble in H_2O, and generally are similar structurally to ethers. Unlike ethers, acetals are hydrolyzed by acids into their respective aldehydes. $H(R)CO + (HO\cdot C_2H_5)_2 \longrightarrow H(R)C(OC_2H_5)_2 + H_2O$. Representative acetals include: $CH_2(OCH_3)_2$, methylene dimethyl ether, bp 42°C; $CH_3CH\ (OCH_3)_2$, ethylidene dimethyl ether, bp 64°C; and $CH_3CH(OC_2H_5)_2$, ethylidene diethyl ether, bp 104°C.

ACETAL RESINS. See **Resins (Acetal)**.

ACETATE DYE. One group comprises water insoluble azo or anthraquinone dyes that have be highly dispersed to make them capable of penetrating and dyeing acetate fibers. A second class consists of water-insoluble amino azo dyes that are made water soluble by treatment with formaldehyde and bisulfite. After absorption by the fiber, the resulting sulfonic acids hydrolyze and regenerate the insoluble dyes.

See also **Dye and Dye Intermediates**; and **Dyes: Anthraquinone**.

ACETATE FIBERS. See **Fibers: Acetate**.

ACETATES. See **Acetic Acid**; **Fibers: Acetate**.

ACETIC ACID. [CAS: 64-19-7]. CH_3COOH, formula weight 60.05, colorless, acrid liquid, mp 16.7°C, bp 118.1°C, sp gr 1.049. Also known as ethanoic acid or vinegar acid, this compound is miscible with H_2O, alcohol, and ether in all proportions. Acetic acid is available commercially in several concentrations. The CH_3COOH content of glacial acetic is approximately 99.7% with H_2O, the principal impurity. Reagent acetic acid generally contains 36% CH_3COOH by weight. Standard commercial aqueous solutions are 28, 56, 70, 80, 85, and 90% CH_3COOH. Acetic acid is the active ingredient in vinegar in which the content ranges from 4 to 5% CH_3COOH. Acetic acid is classified as a weak, monobasic acid. The three hydrogen atoms linked to one of the two carbon atoms are not replaceable by metals.

In addition to the large quantities of vinegar produced, acetic acid in its more concentrated forms is an important high-tonnage industrial chemical, both as a reactive raw and intermediate material for various organic syntheses and as an excellent solvent. Acetic acid is required in the production of several synthetic resins and fibers, pharmaceuticals, photographic chemicals, flavorants, and bleaching and etching compounds.

Early commercial sources of acetic acid included (1) the combined action of *Bacterium aceti* and air on ethyl alcohol in an oxidation-fermentation process: $C_2H_5OH + O_2 \longrightarrow CH_3COOH + H_2O$, the same reaction which occurs when weak alcoholic beverages, such as beer or wine, are exposed to air for a prolonged period and which turn sour because of the formation of acetic acid; and (2) the destructive distillation of wood. A number of natural vinegars still are made by fermentation and marketed as the natural product, but diluted commercially and synthetically produced acetic acid is a much more economic route to follow. The wood distillation route was phased out because of shortages of raw materials and the much more attractive economy of synthetic processes.

The most important synthetic processes are (1) the oxidation of acetaldehyde, and (2) the direct synthesis from methyl alcohol and carbon monoxide. The latter reaction must proceed under very high pressure (approximately 650 atmospheres) and at about 250°C. The reaction takes place in the liquid phase and dissolved cobaltous iodide is the catalyst. $CH_3OH + CO \longrightarrow CH_3COOH$ and $CH_3OCH_3 + H_2O + 2CO \longrightarrow 2CH_3COOH$. The crude acid produced first is separated from the catalyst and then dehydrated and purified in an azeotropic distillation column. The final product is approximately 99.8% pure CH_3COOH.

Acetic acid solution reacts with alkalis to form acetates, e.g., sodium acetate, calcium acetate; similarly, with some oxides, e.g., lead acetate; with carbonates, e.g., sodium acetate, calcium acetate, magnesium acetate; with some sulfides, e.g., zinc acetate, manganese acetate. Ferric acetate solution, upon boiling, yields a red precipitate of basic ferric acetate. Acetic acid solution attacks many metals, liberating hydrogen and forming acetate, e.g., magnesium, zinc, iron. Acetic acid is an important organic substance, with alcohols forming esters (acetates); with phosphorus trichloride forming acetyl chloride $CH_3CO{\cdot}Cl$, which is an important reagent for transfer of the acetyl (CH_3CO-) group; forming acetic anhydride, also an acetyl reagent; forming acetone and calcium carbonate when passed over lime and a catalyzer (barium carbonate) or when calcium acetate is heated; forming methane (and sodium carbonate) when sodium acetate is heated with NaOH; forming mono-, di-, trichloroacetic (or bromoacetic) acids by reaction with chlorine (or bromine) from which hydroxy- and amino-, aldehydic-, dibasic acids, respectively, may be made; forming acetamide when ammonium acetate is distilled. Acetic acid dissolves sulfur and phosphorus, is an important solvent for organic substances, and causes painful wounds when it comes in contact with the skin. Normal acetates are soluble, basic acetates insoluble. The latter are important in their compounds with lead, and copper ("verdigris").

A large number of acetic acid esters are important industrially, including methyl, ethyl, propyl, butyl, amyl, and cetyl acetates; glycol mono- and diacetate; glyceryl mono-, di-, and triacetate; glucose pentacetate; and cellulose tri-, tetra-, and pentacetate.

Acetates may be detected by formation of foul-smelling cacodyl (poisonous) on heating with dry arsenic trioxide. Other tests for acetate are the lanthanum nitrate test in which a blue or bluish-brown ring forms when a drop of 2.5% $La(NO_3)_3$ solution, a drop of 0.01-N iodine solution, and a drop of 0.1% NH_4OH solution are added to a drop of a neutral acetate solution; the ferric chloride test, in which a reddish color is produced by the addition of 1-*N* ferric chloride solution to a neutral solution of acetate; and the ethyl acetate test, in which ethyl alcohol and H_2SO_4 are added to the acetate solution and warmed to form a colorless solution.

Additional Reading

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ACETOACTETIC ESTER CONDENSATION. A class of reactions occasioned by the dehydrating power of metallic sodium or sodium ethoxide on the ethyl esters of monobasic aliphatic acids and a few other esters. It is best known in the formation of acetoacetic ester:

$$\begin{aligned}&2\ CH_3\cdot COOC_2H_5 + 2\ CH_3\cdot COOC_2H_5 + 2\ Na \longrightarrow\\ &\qquad 2\ CH_3\cdot C(ONa):CH\cdot COOC_2H_5 + 2\ C_2H_5OH + H_2\end{aligned}$$

The actual course of the reaction is complex. By the action of acids the sodium may be eliminated from the first product of the reaction and the free ester obtained. This may exist in the tautomeric enol and keto forms ($CH_3\cdot COH{:}CH\cdot COOC_2H_5$ and $CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5$).

On boiling ester with acids or alkalies it will split in two ways, the circumstances determining the nature of the main product. Thus, if moderately strong acid or weak alkali is employed, acetone is formed with very little acetic acid (ketone splitting). In the presence of strong alkalies, however, very little acetone and much acetic acid result (acid splitting). Derivatives of acetoacetic ester may be decomposed in the same fashion, and this fact is responsible for the great utility of this condensation in organic synthesis. This is also due to the reactivity of the $\cdot\ CH_2\cdot$ group, which reacts readily with various groups, notably halogen compounds. Usually the sodium salt of the ester is used, and the condensation is followed by decarboxylation with dilute alkali, or deacylation with concentrated alkali.

$$\begin{aligned}&CH_3\cdot CO\cdot CHNa\cdot COOC_2H_5 + RI \longrightarrow CH_3\cdot CO\cdot CHR\cdot COOC_2H_5\\ &\qquad + NaI\end{aligned}$$

$$\begin{aligned}&CH_3\cdot CO\cdot CHR\cdot COOC_2H_5 \xrightarrow[\text{Dilutealkali}]{H_2O} CH_3\cdot CO\cdot CH_2R\\ &\qquad + C_2H_5OH + CO_2\end{aligned}$$

$$\begin{aligned}&CH_3\cdot CO\cdot CHR\cdot COOC_2H_5 \xrightarrow[\text{Concentrated alkali}]{2\ H_2O} HOOC\cdot CH_2\cdot R\\ &\qquad + C_2H_5OH + CH_3COOH\end{aligned}$$

ACETONE. [CAS: 67-64-1]. $CH_3\cdot CO\cdot CH_3$, formula weight 58.08, colorless, odorous liquid ketone, mp −94.6°C, bp 56.5°C, sp gr 0.792. Also known as dimethyl ketone or propanone, this compound is miscible in all proportions with H_2O, alcohol, or ether. Acetone is a very important solvent and is widely used in the manufacture of plastics and lacquers. For storage purposes, acetylene may be dissolved in acetone. A high-tonnage chemical, acetone is the starting ingredient or intermediate for numerous organic syntheses. Closely related, industrially important compounds are diacetone alcohol (DAA) $CH_3\cdot CO\cdot CH_2\cdot COH(CH_3)_2$ which is used as a solvent for cellulose acetate and nitrocellulose, as well as for various resins and gums, and as a thinner for lacquers and inking materials. Sometimes DAA is mixed with castor oil for use as a hydraulic brake fluid for which its physical properties are well suited, mp −54°C, bp 166°C, sp gr 0.938. A product known as synthetic methyl acetone is prepared by mixing acetone (50%), methyl acetate (30%), and methyl alcohol (20%) and is used widely for coagulating latex and in paint removers and lacquers.

In older industrial processes, acetone is prepared (1) by passing the vapors of acetic acid over heated lime. In a first step, calcium acetate is produced, followed by a breakdown of the acetate into acetone and calcium carbonate:

$$CH_3\cdot CO\cdot O\cdot Ca\cdot OOC\cdot CH_3 \longrightarrow CH_3\cdot CO\cdot CH_3 + CaCO_3;$$

and (2) by fermentation of starches, such as maize, which produce acetone along with butyl alcohol. Modern industrial processes include (3) the use of cumene as a chargestock, in which cumene first is oxidized to cumene hydroperoxide (CHP), this followed by the decomposition of CHP into acetone and phenol; and (4) by the direct oxidation of propylene, using air and catalysts. The catalyst solution consists of copper chloride and small amounts of palladium chloride. The reaction: $CH_3CH = CH_2 + 1/2\ O_2 \longrightarrow CH_3COCH_3$. During the reaction, the palladium chloride is reduced to elemental palladium and HCl. Reoxidation is effected by cupric chloride. The cuprous chloride resulting is reoxidized during the catalyst regeneration cycle. The process is carried out under moderate pressure at about 100°C.

Acetone reacts with many chemicals in a marked manner: (1) with phosphorus pentachloride, yields acetone chloride $(CH_3)_2CCl_2$, (2) with hydrogen chloride dry, yields both mesityl oxide $CH_3COCH{:}C(CH_3)_2$, liquid, bp 132°C, and phorone $(CH_3)_2C{:}CHCOCH{:}\ C(CH_3)_2$, yellow solid, mp 28°C, (3) with concentrated H_2SO_4, yields mesitylene $C_6H_3(CH_3)_3$ (1,3,5), (4) with NH_3, yields acetone amines, e.g., diacetoneamine $C_6H_{12}ONH$, (5) with HCN, yields acetone cyanohydrin $(CH_3)_2CHOH\cdot CN$, readily converted into alpha-hydroxy acid $(CH_3)_2CHOH\cdot COOH$, (6) with sodium hydrogen sulfite, forms acetone-sodiumbisulfite $(CH_3)_2\ COH\cdot SO_3Na$ white solid, from which acetone is readily recoverable by treatment with sodium carbonate solution, (7) with hydroxylamine hydrochloride, forms acetoxime $(CH_3)_2C{:}NOH$, solid, mp 60°C, (8) with phenylhydrazine, yields acetonephenyl-hydrazone $(CH_3)_2C{:}NNHC_6\ H_5\cdot H_2O$, solid, mp 16°C, anhydrous compound, mp 42°C, (9) with semicarbazide, forms acetonesemicarbazone $(CH_3)C{:}NNHCONH_2$, solid, mp 189°C, (10) with magnesium methyl iodide in anhydrous ether ("Grignard's solution"), yields, after reaction with H_2O, trimethylcarbinol $(CH_3)_3COH$, a tertiary alcohol, (11) with ethyl thioalcohol and hydrogen chloride dry, yields mercaptol $(CH_3)_2C(SC_2H_5)_2$, (12) with hypochlorite, hypobromite, or hypoiodite solution, yields chloroform $CHCl_3$, bromoform $CHBr_3$ or iodoform CHI_3, respectively, (13) with most reducing agents, forms isopropyl alcohol $(CH_3)_2CHOH$, a secondary alcohol, but with sodium amalgam forms pinacone $(CH_3)_2COH\cdot COH(CH_3)_2$ (14) with sodium dichromate and H_2SO_4, forms acetic acid CH_3COOH plus CO_2. When acetone vapor is passed through a tube at a dull red heat, ketene $CH_2{:}CO$ and methane CH_4 are formed.

ACETYL CHLORIDE. See **Chlorinated Organics**.

ACETYLENE. [CAS: 74-86-2]. CH:CH formula weight 26.04, mp −81.5°C, bp −84°C, sp gr 0.905 (air = 1.000). Sometimes referred to as ethyne, ethine, or gaseous carbon (92.3% of the compound is C), acetylene is moderately soluble in H_2O or alcohol, and exceptionally soluble in acetone (300 volumes of acetylene in 1 volume of acetone at 12 atmospheres pressure). The gas burns when ignited in air with a luminous sooty flame, requiring a specially devised burner for illumination purposes. An explosive mixture is formed with air over a wide range (about 3 to 80% acetylene), but safe handling is improved when the gas is dissolved in acetone. The heating value is 1455 Btu/ft^3 (8.9 Cal/m^3).

Although acetylene still is used in a number of organic syntheses on an industrial scale, its use on a high-tonnage basis has diminished because of the lower cost of other starting materials, such as ethylene and propylene. Acetylene has been widely used in the production of halogen derivatives, acrylonitrile, acetaldehyde, and vinyl chloride. Within recent years, producers of acrylonitrile switched to propylene as a starting material.

Commercially, acetylene is produced from the pyrolysis of naphtha in a two-stage cracking process. Both acetylene and ethylene are end products. The ratio of the two products can be changed by varying the naphtha feed rate. Acetylene also has been produced by a submerged-flame process from crude oil. In essence, gasification of the crude oil occurs by means of the flame, which is supported by oxygen beneath the surface of the oil. Combustion and cracking of the oil take place at the boundaries of the flame. The composition of the cracked gas includes about 6.3% acetylene and 6.7% ethylene. Thus, further separation and purification are required. Several years ago when procedures were developed for the safe handling of acetylene on a large scale, J. W. Reppe worked out a series of reactions that later became known as "Reppe chemistry." These reactions were particularly important to the manufacture of many high polymers and other synthetic products. Reppe and his associates were able to effect synthesis of chemicals that had been commercially unavailable. An example is the synthesis of cyclooctatetraene by heating a solution of acetylene under pressure in tetrahydrofuran in the presence of a nickel cyanide catalyst. In another reaction, acrylic acid was produced from CO and H_2O in the presence of a nickel catalyst: $C_2H_2 + CO + H_2O \longrightarrow CH_2 : CH \cdot COOH$. These two reactions are representative of a much larger number of reactions, both those that are straight-chain only, and those involving ring closure.

Acetylene reacts (1) with chlorine, to form acetylene tetrachloride $C_2H_2Cl_4$ or $CHCl_2 \cdot CHCl_2$ or acetylene dichloride $C_2H_2Cl_2$ or CHCl:CHCl, (2) with bromine, to form acetylene tetrabromide $C_2H_2Br_4$ or $CHBr_2 \cdot CHBr_2$ or acetylene dibromide $C_2H_2Br_2$ or CHBr:CHBr, (3) with hydrogen chloride (bromide, iodide), to form ethylene monochloride CH_2:CHCl (monobromide, monoiodide), and 1,1-dichloroethane, ethylidene chloride $CH_3 \cdot CHCl_2$ (dibromide, diiodide), (4) with H_2O in the presence of a catalyzer, e.g., mercuric sulfate, to form acetaldehyde $CH_3 \cdot CHO$, (5) with hydrogen, in the presence of a catalyzer, e.g., finely divided nickel heated, to form ethylene C_2H_4 or ethane C_2H_6, (6) with metals, such as copper or nickel, when moist, also lead or zinc, when moist and unpurified. Tin is not attacked. Sodium yields, upon heating, the compounds C_2HNa and C_2Na_2. (7) With ammoniocuprous (or silver) salt solution, to form cuprous (or silver) acetylide C_2Cu_2, dark red precipitate, explosive when dry, and yielding acetylene upon treatment with acid, (8) with mercuric chloride solution, to form trichloromercuric acetaldehyde $C(HgCl)_3 \cdot CHO$, precipitate, which yields with HCl acetaldehyde plus mercuric chloride.

Additional Reading

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ACETYLENE SERIES. A series of unsaturated hydrocarbons having the general formula C_nH_{2n-2}, and containing a triple bond between two carbon atoms. The series is named after the simplest compound of the series, acetylene HC:CH. In more modern terminology, this series of compounds is termed the *alkynes.* See also **Alkynes**.

ACETYLSALICYLIC ACID. [CAS: 50-78-2]. $C_6H_4(COOH)CO_2CH_3$, formula wt, 180.06, mp 133.5°C, colorless, crystalline, slightly soluble in water, soluble in alcohol and ether, commonly known as aspirin, also called orthoacetoxybenzoic acid. The substance is commonly used as a relief for mild forms of pain, including headache and joint and muscle pain. The drug tends to reduce fever. Aspirin and other forms of salicylates have been used in large doses in acute rheumatic fever, but must be administered with extreme care in such cases by a physician. Commercially available aspirin is sometime mixed with other pain relievers as well as buffering agents.

See also **Aspirin**; and **Salicylic Acid and Related Compounds**.

ACHLORHYDRIA. Lack of hydrochloric acid in the digestive juices in the stomach. Hydrochloric acid helps digest food. The low pH of the normal stomach contents is a barrier to infection by various organisms and, where achlorhydria develops—particularly in malnutrition—it renders the patient more susceptible to infection, such as by *Vibrio cholerae* and *Giardia lamblia.* The condition is relatively common among people of about 50 years of age and older, affecting 15 to 20% of the population in this age group. The acid deficiency also occurs in about 30% of patients with adult onset-type of primary hypogamma-globulinemia. A well-balanced diet of easily digestible foods minimizes the discomforting effects of complete absence of hydrochloric acid in the stomach. The condition does not preclude full digestion of fats and proteins, the latter being attacked by intestinal and pancreatic enzymes. In rare cases, where diarrhea may result from achlorhydria, dilute hydrochloric acid may be administered by mouth. Where this causes an increase in discomfort or even pain, the use of dexamethasone or mucosal coating agents is preferred.

Commonly, achlorhydria may not be accompanied by other diseases, but in some cases there is a connection. For example, achlorhydria is an abnormality that sometimes occurs with severe iron deficiency. Histalog-fast achlorhydria, resulting from intrinsic factor deficiency in gastric juice, may be an indication of pernicious anemia. Hyperplastic polyps are often found in association with achlorhydria.

Excessive alcohol intake can also lead to achlorhydria and it is said that the resistance for cyanide poisoning of the Russian mystic, Rasputin, was attributable to that effect. The great amount of vodka that he consumed led to achlorhydria and thus the ingested potassium cyanide did not liberate lethal hydrocyanic gas, nor was the potassium salt absorbed through the stomach walls.

Additional Reading

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ACID-BASE REGULATION (Blood). The hydrogen ion concentration of the blood is maintained at a constant level of pH 7.4 by a complex system of physico-chemical processes, involving, among others, neutralization, buffering, and excretion by the lungs and kidneys. This topic is sometimes referred to as *acid-base metabolism.* The clinical importance of acids and bases in life processes derives from several fundamental factors. (1) Most chemical reactions within the body take place in water solutions. The type and rate of such reactions is seriously affected by acid-base concentrations, of which pH is one indication. (2) Hydrogen ions are mobile charged particles and the distribution of such ions as sodium, potassium, and chloride in the cell environment are ultimately affected by hydrogen ion concentration (pH). (3) It also has been established that hydrogen ion concentration influences the three-dimensional configurations of proteins. Protein conformational changes affect the biochemical activity of proteins and thus can affect normal protein function. For example, enzymes, a particular class of proteins, exhibit optimal activity within a narrow range of pH. Most physiological activities, and especially muscular exercise, are accompanied by the production of acid, to neutralize which, a substantial alkali reserve, mainly in the form of bicarbonate, is maintained in the plasma, and so long as the ratio of carbon dioxide to bicarbonate remains constant, the hydrogen ion concentration of the blood does not alter. Any non-volatile acid, such as lactic or phosphoric, entering the blood reacts with the bicarbonate of the alkali reserve to form carbon dioxide, which is volatile, and which combines with hemoglobin by which it is transported to the lungs and eliminated by the processes of respiration. It will also be evident from this that no acid stronger than carbon dioxide can exist in the blood. The foregoing neutralizing and buffering effects of bicarbonate and hemoglobin are short-term effects; to insure final elimination of excess acid or alkali, certain vital reactions come into play. The rate and depth of respiration are governed by the level of carbon dioxide in the blood, through the action of the respiratory center in the brain; by this means the pulmonary ventilation rate is continually adjusted to secure adequate elimination of carbon dioxide. In the kidneys two mechanisms operate; ammonia is formed, whereby acidic substances in process of excretion are neutralized, setting free basic ions such as sodium to return to the blood to help maintain the alkali reserve. Where there is a tendency toward development of increased acidity in the blood, the kidneys are able selectively to re-absorb sodium bicarbonate from the urine being excreted, and to release into it acid sodium phosphate; where there is a tendency toward alkalemia, alkaline sodium phosphate is excreted, the hydrogen ions thus liberated are re-absorbed to restore the diminishing hydrogen ion concentration. See also **Achlorhydria**; **Acidosis**; **Alkalosis**; **Blood**; **pH (Hydrogen Ion Concentration)**; and **Potassium and Sodium (In Biological Systems)**.

ACIDIC SOLVENT. A solvent which is strongly protogenic, i.e., which has a strong tendency to donate protons and little tendency to accept them. Liquid hydrogen chloride and hydrogen fluoride are acidic solvents, and in them even such normally strong acids as nitric acid do not exhibit acidic properties, since there are no molecules that can accept protons; but, on the contrary, behave to some extent as bases by accepting protons yielded by the dissociation of the HCl or the HF. See **Acids and Bases**.

ACIDIMETRY. An analytical method for determining the quantity of acid in a given sample by titration against a standard solution of a base, or, more broadly, a method of analysis by titration where the end point is recognized by a change in pH (hydrogen ion concentration). See also **Analysis (Chemical)**; **pH (Hydrogen Ion Concentration)**; **Titration (Potentiometric)**; and **Titration (Thermometric)**.

ACIDITY. The amount of acid present, expressed for a solution either as the molecular concentration of acid, in terms of normality, molality, etc., or the ionic concentration (hydrogen ions or protons) in terms of pH (the logarithm of the reciprocal of the hydrogen ion concentration). The acidity of a base is the number of molecules of monoatomic acid which one molecule of the base can neutralize. See **Acids and Bases**.

ACID NUMBER. A term used in the analysis of fats or waxes to designate the number of milligrams of potassium hydroxide (KOH) required to neutralize the free fatty acids in 1 gram of substance. The determination is performed by titrating an alcoholic solution of the wax or fat with tenth or half-normal alkali, using phenolphthalein as indicator.

ACIDOSIS. A condition of excess acidity (or depletion of alkali) in the body, in which acids are absorbed or formed in excess of their elimination, thus increasing the hydrogen ion concentration of the blood, exceeding the normal limit of 7.4. The acidity-alkalinity ratio in body tissue normally is delicately controlled by several mechanisms, notably the regulation of carbon dioxide-oxygen transfer in the lungs, the presence of buffer compounds in the blood, and the numerous sensing areas that are a part of the central nervous system. Normally, acidic materials are produced in excess in the body, this excess being neutralized by the presence of free alkaline elements, such as sodium occurring in plasma. The combination of sodium with excess acids produces carbon dioxide which is exhaled. Acidosis may result from: (1) severe exercise, leading to increased carbon dioxide content of the blood, (2) sleep, especially under narcosis, where the elimination of carbon dioxide is depressed, (3) heart failure, where there is diminished ventilation of carbon dioxide through the lungs, (4) diabetes and starvation, in which organic acids, such as β-hydroxybutyric and acetoacetic acids, accumulate, (5) kidney failure, in which the damaged kidneys cannot excrete acid radicals, and (6) severe diarrhea, in which there is loss of alkaline substances. Nausea, vomiting, and weakness sometimes may accompany acidosis. See also **Acid-Base Regulation (Blood)**; **Blood**; and **Potassium and Sodium (In Biological Systems)**.

ACID RAIN. Acid rain can be simply described as rain that is more acidic than normal. Acid rain is a complicated problem. Caused by air pollution, acid rain's spread and damage involve weather, chemistry, soil, and the life cycles of plants and animals on the land and in the water.

Scientists have discovered that air pollution from the burning of fossil fuels is the major cause of acid rain. Acidic deposition, or acid rain, as it is commonly known, occurs when emissions of sulfur dioxide (SO_2) and oxides of nitrogen (NO_X) react in the atmosphere with water, oxygen, and oxidants to form various acidic compounds. This mixture forms a mild solution of sulfuric acid and nitric acid. Sunlight increases the rate of most of these reactions.

These compounds then fall to the earth in either wet form (such as rain, snow, and fog or dry form (such as gas and particles). About half of the acidity in the atmosphere falls back to earth through dry deposition as gases and dry particles. The wind blows these acidic particles and gases onto buildings, cars, homes, and trees. In some instances, these gases and particles can eat away the things on which they settle. Dry deposited gases and particles are sometimes washed from trees and other surfaces by rain. When that happens, the runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone. The combination of acid rain plus dry deposited acid is called *acid deposition*. See **Acid Deposition**, which is discussed in more detail later in this entry. Prevailing winds transport the compounds, sometimes hundreds of miles, across state and national borders.

Electric utility plants account for about 70 percent of annual SO_2 emissions and 30 percent of NO_X emissions in the United States. Mobile sources (transportation) also contribute significantly to NO_X emissions. Overall, over 20 million tons of SO_2 and NO_X are emitted into the atmosphere each year.

Acid rain causes acidification of lakes and streams and contributes to damage of trees at high elevations (for example, red spruce trees above 2,000 feet in elevation). In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage. Prior to falling to the earth, SO_2 and NO_X gases and their particulate matter derivatives, sulfates and nitrates, contribute to visibility degradation and impact public health.

Implementation of the Acid Rain Program under the 1990 Clean Air Act Amendments will confer significant benefits on the nation. By reducing SO_2 and NO_X, many acidified lakes and streams will improve substantially so that they can once again support fish life. Visibility will improve, allowing for increased enjoyment of scenic vistas across our country, particularly in National Parks. Stress to the forests that populate the ridges of mountains from Maine to Georgia will be reduced. Deterioration of historic buildings and monuments will be slowed. Finally, reductions in SO_2 and NO_X will reduce sulfates, nitrates, and ground level ozone (smog), leading to improvements in public health.

Surface Waters

Acid rain primarily affects sensitive bodies of water, that is, those that rest atop soil with a limited ability to neutralize acidic compounds (called "buffering capacity"). Many lakes and streams examined in a National Surface Water Survey (NSWS) suffer from chronic acidity, a condition in which water has a constant low (acidic) pH level. The survey investigated the effects of acidic deposition in over 1,000 lakes larger than 10 acres and in thousands of miles of streams believed to be sensitive to acidification. Of the lakes and streams surveyed in the NSWS, acid rain has been determined to cause acidity in 75 percent of the acidic lakes and about 50 percent of the acidic streams. Several regions in the U.S. were identified as containing many of the surface waters sensitive to acidification. They include, but are not limited to, the Adirondacks, the mid-Appalachian highlands, the upper Midwest, and the high elevation West.

In some sensitive lakes and streams, acidification has completely eradicated fish species, such as the brook trout, leaving these bodies of water barren. In fact, hundreds of the lakes in the Adirondacks surveyed in the NSWS have acidity levels indicative of chemical conditions unsuitable for the survival of sensitive fish species.

Emissions from U.S. sources also contribute to acidic deposition in eastern Canada, where the soil is very similar to the soil of the Adirondack Mountains, and the lakes are consequently extremely vulnerable to chronic acidification problems. The Canadian government has estimated that 14,000 lakes in eastern Canada are acidic.

Streams flowing over soil with low buffering capacity are equally as susceptible to damage from acid rain as lakes are. Approximately 580 of the streams in the Mid-Atlantic Coastal Plain are acidic primarily due to acidic deposition. The New Jersey Pine Barrens area endures the highest rate of acidic streams in the nation with over 90 percent of the streams acidic. Over 1,350 of the streams in the Mid-Atlantic Highlands (mid-Appalachia) are acidic, primarily due to acidic deposition. Many streams in that area have already experienced trout losses due to the rising acidity.

Acidification is also a problem in surface water populations that were not surveyed in federal research projects. For example, although lakes smaller than 10 acres were not included in the NSWS, there are from one to four times as many of these small lakes as there are larger lakes. In the Adirondacks, the percentage of acidic lakes is significantly higher when it includes smaller lakes (26 percent) than when it includes only the target size lakes (14 percent).

The acidification problem in both the United States and Canada grows in magnitude if "episodic acidification" (brief periods of low pH levels from snowmelt or heavy downpours) is taken into account. Lakes and streams throughout the United States, including high-elevation western lakes, are sensitive to episodic acidification. In the Mid-Appalachians, the Mid-Atlantic Coastal Plain, and the Adirondack Mountains, many additional lakes and streams become temporarily acidic during storms and snowmelt. Episodic acidification can cause large-scale "fish kills."

For example, approximately 70 percent of sensitive lakes in the Adirondacks are at risk of episodic acidification. This amount is over three times the amount of chronically acidic lakes. In the mid-Appalachians, approximately 30 percent of sensitive streams are likely to become acidic during an episode. This level is seven times the number of chronically acidic streams in that area.

Acid rain control will produce significant benefits in terms of lowered surface water acidity. If acidic deposition levels were to remain constant over the next 50 years (the time frame used for projection models), the acidification rate of lakes in the Adirondacks that are larger than 10 acres would rise by 50 percent or more. Scientists predict, however, that the decrease in SO_2 emissions required by the Acid Rain Program will significantly reduce acidification due to atmospheric sulfur. Without the reductions in SO_2 emissions, the proportions of aquatic systems in sensitive ecosystems that are acidic would remain high or dramatically worsen.

The impact of nitrogen on surface waters is also critical. Nitrogen plays a significant role in episodic acidification and new research recognizes the importance of nitrogen in long-term chronic acidification as well. Furthermore, the adverse impact of atmospheric nitrogen deposition on estuaries and other large bodies of water may be significant. For example, 30 to 40 percent of the nitrogen in the Chesapeake Bay comes from atmospheric deposition. Nitrogen is an important factor in causing eutrophication (oxygen depletion) of water bodies.

Forests

Acid rain has been implicated in contributing to forest degradation, especially in high-elevation spruce trees that populate the ridges of the Appalachian Mountains from Maine to Georgia, including national park areas such as the Shenandoah and Great Smoky Mountain national parks. Acidic deposition seems to impair the trees' growth in several ways; for example, acidic cloud water at high elevations may increase the susceptibility of the red spruce to winter injury.

There also is a concern about the impact of acid rain on forest soils. There is good reason to believe that long-term changes in the chemistry of some sensitive soils may have already occurred as a result of acid rain. As acid rain moves through the soils, it can strip away vital plant nutrients through chemical reactions, thus posing a potential threat to future forest productivity.

Visibility

Sulfur dioxide emissions lead to the formation of sulfate particles in the atmosphere. Sulfate particles account for more than 50 percent of the visibility reduction in the eastern part of the United States, affecting our enjoyment of national parks, such as the Shenandoah and the Great Smoky Mountains. The Acid Rain Program is expected to improve the visual range in the eastern U.S. by 30 percent. Based on a study of the value national park visitors place on visibility, the visual range improvements expected at national parks of the eastern United States due to the Acid Rain Program's SO_2 reductions will be worth a billion dollars by the year 2010. In the western part of the United States, nitrogen and carbon also play roles, but sulfur has been implicated as an important source of visibility impairment in many of the Colorado River Plateau national parks, including the Grand Canyon, Canyonlands, and Bryce Canyon.

Materials

Acid rain and the dry deposition of acidic particles are known to contribute to the corrosion of metals and deterioration of stone and paint on buildings, cultural objects, and cars. The corrosion seriously depreciates the objects' value to society. Dry deposition of acidic compounds can also dirty buildings and other structures, leading to increased maintenance costs. To reduce damage to automotive paint caused by acid rain and acidic dry deposition, some manufacturers use acid-resistant paints, at an average cost of $5 for each new vehicle (or a total of $61 million per year for all new cars and trucks sold in the U.S.) The Acid Rain Program will reduce damage to materials by limiting SO_2 emissions. The benefits of the Acid Rain Program are measured, in part, by the costs now paid to repair or prevent damage—the costs of repairing buildings, using acid-resistant paints on new vehicles, plus the value that society places on the details of a statue lost forever to acid rain.

Health

Based on health concerns, SO_2 has historically been regulated under the Clean Air Act. Sulfur dioxide interacts in the atmosphere to form sulfate aerosols, which may be transported long distances through the air. Most sulfate aerosols are particles that can be inhaled. In the eastern United States, sulfate aerosols make up about 25 percent of the inhalable particles. According to recent studies at Harvard and New York Universities, higher levels of sulfate aerosols are associated with increased morbidity (sickness) and mortality from lung disorders, such as asthma and bronchitis. By lowering sulfate aerosol levels, the Acid Rain Program will reduce the incidence and the severity of asthma and bronchitis. When fully implemented by the year 2010, the public health benefits of the Acid Rain Program will be significant, due to decreased mortality, hospital admissions, and emergency-room visits.

Decreases in nitrogen oxide emissions are also expected to have positive health effects by reducing the nitrate component of inhalable particulates and reducing the nitrogen oxides available to react with volatile organic compounds (VOCs) and form ozone. Ozone impacts on human health include a number of morbidity and mortality risks associated with lung disorders.

Automotive Coatings

Since about 1990, reports of damage to automotive coatings have increased. The reported damage typically occurs on horizontal surfaces and appears as irregularly shaped, permanently etched areas. The damage can best be detected under fluorescent lamps, can be most easily observed on dark colored vehicles, and appears to occur after evaporation of a moisture droplet. In addition, some evidence suggests damage occurs most frequently on freshly painted vehicles. Usually the damage is permanent; once it has occurred, the only solution is to repaint.

The general consensus within the auto industry is that the damage is caused by some form of environmental fallout. "Environmental fallout," a term widely used in the auto and coatings industries, refers to damage caused by air pollution (e.g., acid rain), decaying insects, bird droppings, pollen, and tree sap. The results of laboratory experiments and at least one field study have demonstrated that acid rain can scar automotive coatings. Furthermore, chemical analyses of the damaged areas of some exposed test panels showed elevated levels of sulfate, implicating acid rain.

The popular term "acid rain" refers to both wet and dry deposition of acidic pollutants that may damage material surfaces, including auto finishes. These pollutants, which are released when coal and other fossil fuels are burned react with water vapor and oxidants in the atmosphere and are chemically transformed into sulfuric and nitric acids. The acidic compounds then may fall to earth as rain, snow, fog, or may join dry particles and fall as dry deposition. Automotive coatings may be damaged by all forms of acid rain, including dry deposition, especially when dry acidic deposition is mixed with dew or rain. However, it has been difficult to quantify the specific contribution of acid rain to paint finish damage relative to damage caused by other forms of environmental fallout, by the improper application of paint or by deficient paint formulations. According to coating experts, trained specialists can differentiate between the various forms of damage, but the best way of determining the cause of chemically induced damage is to conduct a detailed, chemical analysis of the damaged area.

Because evaporation of acidic moisture appears to be a key element in the damage, any steps taken to eliminate its occurrence on freshly painted vehicles may alleviate the problem. The steps include frequent washing followed by hand drying, covering the vehicle during precipitation events, and use of one of the protective coatings currently on the market that claim to protect the original finish. (However, data on the performance of these coatings are not yet sufficient.)

The auto and coatings industries are fully aware of the potential damage and are actively pursuing the development of coatings that are more resistant to environmental fallout, including acid rain. The problem is not a universal one—it does not affect all coatings or all vehicles even in geographic areas known to be subject to acid rain, which suggests that technology exists to protect against this damage. Until that technology is implemented to protect all vehicles or until acid deposition is adequately reduced, frequent washing and drying and covering the vehicle appear to be the best methods to minimize acid rain damage.

Acid Deposition

Sulfur and nitrogen oxides are emitted into the atmosphere primarily from the burning of fossil fuels. These emissions react in the atmosphere to form compounds that are transported long distances and are subsequently deposited in the form of pollutants such as particulate matter (sulfates and nitrates), SO_2, NO_2, nitric acid and when reacted with volatile organic compounds (VOCs) form ozone. The effects of atmospheric deposition include acidification of lakes and streams, nutrient enrichment of coastal waters and large river basins, soil nutrient depletion and decline of sensitive forests, agricultural crop damage, and impacts on ecosystem biodiversity. Toxic pollutants and metals also can be transported and deposited through atmospheric processes.

Both local and long-range emission sources contribute to atmospheric deposition. Total atmospheric deposition is determined using both wet and dry deposition measurements. Although the term "acid rain" is widely recognized, the dry deposition portion ranges from 20 to 60 percent of total deposition.

The United States Environmental Protection agency (EPA) is required by several Congressional and other mandates to assess the effectiveness of air pollution control efforts. These mandates include Title IX of the Clean Air Act Amendments (CAAA), the National Acid Precipitation Assessment Program (NAPAP), the Government Performance and Results

Act, and the U.S. Canada Air Quality Agreement. One measure of effectiveness of these efforts is whether sustained reductions in the amount of atmospheric deposition over broad geographic regions are occurring. However, changes in the atmosphere happen very slowly and trends are often obscured by the wide variability of measurements and climate. Many years of continuous and consistent data are required to overcome this variability, making long-term monitoring networks especially critical for characterizing deposition levels and identifying relationships among emissions, atmospheric loadings, and effects on human health and the environment.

For wet and dry deposition, these studies typically include measurement of concentration levels of key chemical components as well as precipitation amounts. For dry deposition, analyses also must include meteorological measurements that are used to estimate rate of the actual deposition, or "flux." Data representing total deposition loadings (e.g., total sulfate or nitrate) are what many environmental scientists use for integrated ecological assessments.

Primary Atmospheric Deposition Monitoring Networks

The National Atmospheric Deposition Program (NADP) and the Clean Air Status and Trends Network (CASTNET), described in detail below, were developed to monitor wet and dry acid deposition, respectively. Monitoring site locations are predominantly rural by design to assess the relationship between regional pollution and changes in regional patterns in deposition. CASTNET also includes measurements of rural ozone and the chemical constituents of $PM_{2.5}$. Rural monitoring sites of NADP and CASTNET provide data where sensitive ecosystems are located and provide insight into natural background levels of pollutants where urban influences are minimal. These data provide needed information to scientists and policy analysts to study and evaluate numerous environmental effects, particularly those caused by regional sources of emissions for which long-range transport plays an important role. Measurements from these networks are also important for understanding non-ecological impacts of air pollution such as visibility impairment and damage to materials, particularly those of cultural and historical importance.

National Atmospheric Deposition Network

The NADP was initiated in the late 1970s as a cooperative program between federal and state agencies, universities, electric utilities, and other industries to determine geographical patterns and trends in precipitation chemistry in the United States. Collection of weekly wet deposition samples began in 1978. The size of the NADP Network grew rapidly in the early 1980s when the major research effort by the NAPAP called for characterization of acid deposition levels. At that time, the network became known as the NADP/NTN (National Trends Network). By the mid-1980s, the NADP had grown to nearly 200 sites, where it stands today, as the longest running national deposition monitoring network.

The NADP analyzes the constituents important in precipitation chemistry, including those affecting rainfall acidity and those that may have ecological effects. The Network measures sulfate, nitrate, hydrogen ion (measure of acidity), ammonia, chloride, and base cations (calcium, magnesium, potassium). To ensure comparability of results, laboratory analyses for all samples are conducted by the NADP's Central Analytical Lab at the Illinois State Water Survey. A new subnetwork of the NADP, the Mercury Deposition Network (MDN) measures mercury in precipitation.

Clean Air Status and Trends Network

The CASTNET provides atmospheric data on the dry deposition component of total acid deposition, ground-level ozone, and other forms of atmospheric pollution. CASTNET is considered the nation's primary source for atmospheric data to estimate dry acidic deposition and to provide data on rural ozone levels. Used in conjunction with other national monitoring networks, CASTNET is used to determine the effectiveness of national emission control programs. Established in 1987, CASTNET now comprises over 70 monitoring stations across the United States. The longest data records are primarily at eastern sites. The majority of the monitoring stations are operated by EPA's Office of Air and Radiation; however, approximately 20 stations are operated by the National Park Service in cooperation with EPA.

Each CASTNET dry deposition station measures:

- weekly average atmospheric concentrations of sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid.
- hourly concentrations of ambient ozone levels.
- meteorological conditions required for calculating dry deposition rates.

Dry deposition rates are calculated using atmospheric concentrations, meteorological data, and information on land use, vegetation, and surface conditions. CASTNET complements the database complied by NADP. Because of the interdependence of wet and dry deposition, NADP wet deposition data are collected at all CASTNET sites. Together, these two long-term databases provide the necessary data to estimate trends and spatial patterns in total atmospheric deposition. National Oceanic and Atmospheric Administration (NOAA) also operates a smaller dry deposition network called Atmospheric Integrated Assessment Monitoring Network (AIRMoN) focused on addressing research issues specifically related to dry deposition measurement.

Ozone Data Collection Network

Ozone data collected by CASTNET are complementary to the larger ozone data sets gathered by the State and Local Air Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS) networks. Most air-quality samples at SLAMS/NAMS sites are located in urban areas, while CASTNET sites are in rural locations. Hourly ozone measurements are taken at each of the 50 sites operated by EPA. Data from these sites provide information to help characterize ozone transport issues and ozone exposure levels.

Integrated Monitoring, and AIRMoN

The Atmospheric Integrated Research Monitoring Network is an atmospheric component to the overall national integrated monitoring initiative that is currently evolving. AIRMoN is a relatively new program, constructed by combining and building upon pre-existing specialized wet deposition and dry deposition monitoring networks, and with two specific goals:

1. *To provide regular and timely reports on the atmospheric consequences of emission reductions, as imposed under the Clean Air Act Amendments.*
2. *To provide quantified information required to extend these observations of atmospheric effects to atmospheric deposition, both wet and dry.*

AIRMoN has two principal components: wet and dry deposition. All variables are measured in a manner that is designed to detect and properly attribute the benefits of emissions controls mandated under the Clean Air Act Amendments of 1990, and to reveal the actual deposition that occurred without fear of chemical (or other) contamination. It should be emphasized that conventional monitoring programs rely on statistical methods to extract small signals from imperfect and noisy data records. AIRMoN is designed to take a new step, that will remove much of the noise by integrating modern forecast technology into the monitoring process.

ARL presently focuses its research attention on:

- the measurement of precipitation chemistry with fine time resolution (AIRMoN-wet),
- the development of systems for measuring deposition, both wet and dry,
- the measurement of dry deposition using micrometeorological methods (AIRMoN-dry),
- the development of techniques for assessing air-surface exchange in areas (such as specific watersheds) where intensive studies are not feasible, and
- the extension of local measurements and knowledge to describe a real average exchange in numerical models.

Clean Air Act

The overall goal is to achieve significant environmental and public health benefits through reductions in emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_X), the primary causes of acid rain. To achieve this goal at the lowest cost to society, the program employs both traditional and innovative, market-based approaches for controlling air pollution. In addition, the program encourages energy efficiency and pollution prevention.

Title IV of the Clean Air Act Amendments of 1990 calls for a 10 million ton reduction in annual emissions of sulfur dioxide (SO_2) in the United States by the year 2010, which represents an approximately 40 percent reduction in anthropogenic emissions from 1980 levels. Implementation of Title IV is referred to as the Acid Rain Program; the primary motivation for this section of the Clean Air Act Amendments is to reduce acid precipitation and dry deposition. To achieve these reductions, the law requires a two-phase tightening of the restrictions placed on fossil-fuel-fired power plants.

The Act also calls for a 2 million ton reduction in NO_X emissions by the year 2000. A significant portion of this reduction will be achieved by coal-fired utility boilers that will be required to install low NO_X burner technologies and to meet new emissions standards.

Phase I began in 1995 and affects 263 units at 110 mostly coal-burning electric utility plants located in 21 eastern and midwestern states. An additional 182 units joined Phase I of the program as substitution or compensating units, bringing the total of Phase I affected units to 445. Emissions data indicate that 1995 SO_2 emissions at these units nationwide were reduced by almost 40% below their required level.

Phase II, which begins in the year 2000, tightens the annual emissions limits imposed on these large, higher emitting plants and also sets restrictions on smaller, cleaner plants fired by coal, oil, and gas, encompassing over 2,000 units in all. The program affects existing utility units serving generators with an output capacity of greater than 25 megawatts and all new utility units.

See also **Pollution (Air)**.

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ACIDS AND BASES. The conventional definition of an acid is that it is an electrolyte that furnishes protons, i.e., hydrogen ions, H^+. An acid is sour to the taste and usually quite corrosive. A base is an electrolyte that furnishes hydroxyl ions, OH^-. A base is bitter to the taste and also usually quite corrosive. These definitions were formulated in terms of water solutions and, consequently, do not embrace situations where some ionizing medium other than water may be involved. In the definition of Lowry and Brnsted, an acid is a proton donor and a base is a proton acceptor. Acid-base theory is described later.

Acidification is the operation of creating an excess of hydrogen ions, normally involving the addition of an acid to a neutral or alkaline solution until a pH below 7 is achieved, thus indicating an excess of hydrogen ions. In *neutralization,* a balance between hydrogen and hydroxyl ions is effected. An acid solution may be neutralized by the addition of a base; and vice versa. The products of neutralization are a salt and water.

Some of the inorganic acids, such as hydrochloric acid, HCl, nitric acid, HNO_3, and sulfuric acid, H_2SO_4, are very-high-tonnage products and are considered very important chemical raw materials. The most common inorganic bases (or alkalis) include sodium hydroxide, NaOH, and potassium hydroxide, KOH, and also are high-tonnage materials, particularly NaOH.

Several classes of organic substances are classified as acids, notably the carboxylic acids, the amino acids, and the nucleic acids. These and the previously mentioned materials are described elsewhere in this volume.

Principal theories of acids and bases have included: (1) Arrhenius-Ostwald theory, which was proposed soon after the concept of the *ionization* of chemical substances in aqueous solutions was generally accepted. (2) Much later (1923), J.N. Brønsted defined an acid as a source of protons and a base is an acceptor of protons. (3) T.M. Lowry, working in the same time frame as Brønsted, developed a similar concept and, over the years, the concept has been referred to in the literature as the *Lowry-Brønsted theory*. It will be noted that this theory altered the definition of an acid very little, continuing to emphasize the role of the hydrogen ion. However, the definition of a base was extended beyond the role of the hydroxyl ion to include a wide variety of uncharged species, such as ammonia and the amines. (4) In 1938, G.N. Lewis further broadened the definition of Lowry-Brønsted. Lewis defined an acid as anything that can attach itself to something with an unshared pair of electrons. The broad definition of Lewis creates some difficulties when one attempts to categorize Lewis acids and bases. R.G. Pearson (1963) suggested two main categories—hard and soft acids as well as hard and soft bases. These are described in more detail by Long and Boyd (1983). (5) In 1939, M. Usanovich proposed still another theory called the *positive-negative* theory, also developed in detail by Long and Boyd.

In terms of the definition that an acid is a proton donor and a base is a proton acceptor, hydrochloric acid, water, and ammonia (NH_3) are acids in the reactions

$$HCl \rightleftharpoons H^+ + Cl^-$$

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

$$NH_3 \rightleftharpoons H^+ + NH_2{}^-$$

Note that this definition is different in at least two major respects from the conventional definition of an acid as a substance dissociating to give H^+ in water. The Lowry-Brnsted definition states that for every acid there be a "conjugate" base, and vice versa. Thus, in the examples cited above, Cl^-, OH^-, and NH^--are the conjugate bases of HCl, H_2O, and NH_3.

Furthermore, since the equations given above should more properly be written

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$NH_3 + H_2O \rightleftharpoons H_3O^+ + NH_2{}^-$$

It can be seen that every acid-base reaction involving transfer of a proton will involve two conjugate acid-base pairs, e.g., in the last equation NH_3 and H_3O^+ are the acids and $NH_2{}^-$ and H_2O the respective conjugate bases. On the other hand, in the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

H_2O and $NH_4{}^-$ are the acids and NH_3 and OH^- the bases. In other reactions, e.g.,

$$\begin{array}{llcll}
\mathit{Base}_1 & \mathit{Acid}_2 & & \mathit{Acid}_1 & \mathit{Base}_2 \\
C_2H_3O_2{}^- & + H_2O & \rightleftharpoons & HC_2H_3O_2 & + OH^- \\
HCO_3{}^- & + HCO_3{}^- & \rightleftharpoons & H_2CO_3 & + CO_3{}^{-2} \\
N_2H_5{}^+ & + N_2H_5 + & \rightleftharpoons & N_2H_6{}^{+2} & + N_2H_4 \\
H_2O & + Cr(H_2O)_6{}^{+3} & \rightleftharpoons & N_3O^+ & + Cr(H_2O)_5OH^{2+}
\end{array}$$

the conjugate acids and bases are as indicated. The theory is not limited to the aqueous solution; for example, the following reactions can be considered in exactly the same light:

$$\begin{array}{llcll}
\mathit{Base}_1 & \mathit{Acid}_2 & & \mathit{Acid}_1 & \mathit{Base}_2 \\
NH_3 & + HCl & \rightleftharpoons & NH_4{}^+ & + Cl^- \\
CH_3CO_2H & + HF & \rightleftharpoons & CH_3CO_2H_2{}^+ & + F^- \\
HF & + HClO_4 & \rightleftharpoons & H_2F^+ & + ClO_4{}^- \\
(CH_3)_2O & + HI & \rightleftharpoons & (CH_3)_2OH^+ & + I^- \\
C_6H_6 & + HSO_3F & \rightleftharpoons & C_6H_7{}^+ & + SO_3F^-
\end{array}$$

Acids may be classified according to their charge or lack of it. Thus, in the reactions cited above, there are "molecular" acids and bases, such as HCl, H_2CO_3, $HClO_4$, etc., and N_2H_4, $(CH_3)_2O$, C_6H_6, etc., and also cationic acids and bases, such as H_3O^+, $N_2H_5^+$, $N_2H_6^{2+}$, NH_4^+, $(CH_3)_2OH^+$, etc., as well as anionic acids and bases, such as HCO_3^-, Cl^-, NH_2^-, NH_3^{-2} etc. In a more general definition, Lewis calls a base any substance with a free pair of electrons that it is capable of sharing with an electron pair acceptor, which is called an acid. For example, in the reaction:

$$(C_2H_5)_2O : + BF_3 \longrightarrow (C_2H_5)_2O{:}BF_3$$

the ethyl ether molecule is called a base, the boron trifluroide, an acid. The complex is called a *Lewis salt*, or *addition compound*.

Acids are classified as monobasic, dibasic, tribasic, polybasic, etc., according to the number (one, two, three, several, etc.) of hydrogen atoms, replaceable by bases, contained in a molecule. They are further classified as (1) organic, when the molecule contains carbon; (1a) carboxylic, when the proton is from a—COOH group; (2) normal, if they are derived from phosphorus or arsenic, and contain three hydroxyl groups: (3) ortho, meta, or para, according to the location of the carboxyl group in relation to another substituent in a cyclic compound; or (4) ortho, meta, or pyro, according to their composition.

Superacids. Although mentioned in the literature as early as 1927, superacids were not investigated aggressively until the 1970s. Prior to the concept of superacids, scientists generally regarded the familiar mineral acids (HF, HNO_3, H_2SO_4, etc.) as the strongest acids attainable. Relatively recently, acidities up to 10^{12} times that of H_2SO_4 have been produced.

In very highly concentrated acid solutions, the commonly used measurement of pH is not applicable. See also **pH (Hydrogen Ion Concentration)**. Rather, the acidity must be related to the degree of transformation of a base with its conjugate acid. In the *Hammett acidity function*, developed by Hammett and Deyrup in 1932,

$$H_0 = pK_{BH^+} - \log\frac{BH^+}{B}$$

where $pkBH^+$ is the dissociation constant of the conjugate acid (BH^+), and BH^+/B is the ionization ratio, measurable by spectroscopic means (UV or NMR). In the Hammett acidity function, acidity is a logarithmic scale wherein H_2SO_4 (100%) has an H_0 of -11.9; and HF, an H_0 of -11.0.

As pointed out by Olah et al. (1979), "The acidity of a sulfuric acid solution can be increased by the addition of solutes that behave as acids in the system: $HA + H_2SO_4 \rightleftharpoons H_3SO_4^+ + A^-$. These solutes increase the concentration of the highly acidic H_3SO_4 cation just as the addition of an acid to water increases the concentration of the oxonium ion. H_3O^+. Fuming sulfuric acid (oleum) contains a series of such acids, the polysulfuric acids, the simplest of which is disulfuric acid, $H_2S_2O_7$, which ionizes as a moderately strong acid in sulfuric acid: $H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^- + HS_2O_7^-$. Higher polysulfuric acids, such as $H_2S_3O_{10}$ and $H_2S_4O_{13}$, also behave as acids and appear somewhat stronger than $H_2S_2O_7$."

Hull and Conant in 1927 showed that weak organic bases (ketones and aldehydes) will form salts with perchloric acid in nonaqueous solvents. This results from the ability of perchloric acid in nonaqueous systems to protonate these weak bases. These early investigators called such a system a superacid. Some authorities believe that any protic acid that is stronger than sulfuric acid (100%) should be typed as a superacid. Based upon this criterion, fluorosulfuric acid and trifluoro-methanesulfonic acid, among others, are so classified. Acidic oxides (silica and silica-alumina) have been used as solid acid catalysts for many years. Within the last few years, solid acid systems of considerably greater strength have been developed and can be classified as *solid superacids*.

Superacids have found a number of practical uses. Fluoroantimonic acid, sometimes called *Magic Acid*, is particularly effective in preparing stable, long-lived carbocations. Such substances are too reactive to exist as stable species in less acidic solvents. These acids permit the protonation of very weak bases. For example, superacids, such as Magic Acid, can protonate saturated hydrocarbons (alkanes) and thus can play an important role in the chemical transformation of hydrocarbons, including the processes of isomerization and alkylation. See also **Alkylation**; and **Isomerization**. Superacids also can play key roles in polymerization and in various organic syntheses involving dienone-phenol rearrangement, reduction, carbonylation, oxidation, among others. Superacids also play a role in inorganic chemistry, notably in the case of halogen cations and the cations of nonmetallic elements, such as sulfur, selenium, and tellurium.

Free Hydroxyl Radical. It is important to distinguish the free radical $\cdot OH$ and the OH^- ion previously mentioned. The free radical is created by complex reactions of so-called "excited" oxygen with hydrogen as the result of exposure to solar ultraviolet light. The radical has been found to be an important factor in atmospheric and oceanic chemistry. The life span of the radical is but a second or two, during which time it reacts with numerous atmospheric pollutants in a scavenging (oxidizing) manner. For example, it reacts with carbon monoxide, as commonly encountered in atmospheric smog. It also reacts with sulfurous gases and with hydrocarbons, as may result from incomplete combustion processes or that have escaped into the atmosphere (because of their volatility) from various sources.

Because of the heavy workload placed upon the hydroxyl radical through such "cleansing" reactions in the atmosphere, some scientists are concerned that the atmospheric content of $\cdot OH$ has diminished with increasing pollution, estimating the probable drop to be as much as 5–25% during the past three centuries since the start of the Industrial Revolution. Ironically, some of the very pollutants that are targets for reduction also are compounds from which the $\cdot OH$ radical is produced and, as they are reduced, so will the concentration of $\cdot OH$ be reduced. The fact that there is only one hydroxyl radical per trillion air molecules must not detract from its effectiveness as a scavenger.

Scientists at the Georgia Institute of Technology have devised a mass spectrometric means for testing the various theories pertaining to the chemistry of $\cdot OH$.

The probable importance of $\cdot OH$ in the oceans also is being investigated. Researchers at Washington State University and the Brookhaven National Laboratory have confirmed the presence of $\cdot OH$ in seawater and now are attempting to measure its content quantitatively and to determine the sources of its formation. Dissolved organic matter is one highly suspected source. Tentatively, it has been concluded (using a method called flash photolysis) that $\cdot OH$ concentrations (as well as daughter radicals) range from 5 to 15 times higher in deep water than in open-ocean surface waters. This may indicate that $\cdot OH$ may have some impact on biota residing in deep water and may enhance the secondary production of bacterial growth, particularly in "carbon limited" oligotrophic waters, in upwelling waters, and in regions with high ultraviolet radiation.

See also specific acids and bases, such as sulfuric acid and sodium hydroxide, in alphabetically arranged entries throughout this *Encyclopedia*.

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ACIDULANTS AND ALKALIZERS (Foods). Well over 50 chemical additives are commonly used in food processing or as ingredients of final food products, essentially to control the pH (hydrogen ion concentration) of the process and/or product. An excess of hydrogen ions, as contributed by acid substances, produces a sour taste, whereas an excess of hydroxyl ions, as contributed by alkaline substances, creates a bitter taste. Soft drinks and instant fruit drinks, for example, owe their tart flavor to acidic substances, such as citric acid. Certain candies, chewing gums, jellies, jams, and salad dressings are among the many other products where a certain degree of tartness contributes to the overall taste and appeal.

Taste is only one of several qualities of a process or product that is affected by an excess of either of these ions. Some raw materials are naturally too acidic, others too alkaline—so that neutralizers must be added to adjust the pH within an acceptable range. In the dairy industry, for example, the acid in sour cream must be adjusted by the addition of alkaline compounds in order that satisfactory butter can be churned. Quite often, the pH may be difficult to adjust or to maintain after adjustment. Stability of pH can be accomplished by the addition of buffering agents that, within limits, effectively maintain the desired pH even when additional acid or alkali is added. For example, orange-flavored instant breakfast drink has just enough “bite” from the addition of potassium citrate (a buffering agent) to regulate the tart flavor imparted by another ingredient, citric acid. In some instances, the presence of acids or alkalies assists mechanical processing operations in food preparation. Acids, for example, make it easier to peel fruits and tubers. Alkaline solutions are widely used in removing hair from animal carcasses.

The pH values of various food substances cover a wide range. Plant tissues and fluids (about 5.2); animal tissues and fluids (about 7.0 to 7.5); lemon juice (2.0 to 2.2); acid fruits (3.0 to 4.5); fruit jellies (3.0 to 3.5).

Acidulants commonly used in food processing include: Acetic acid (glacial), citric acid, fumaric acid, glucono delta-lactone, hydrochloric acid, lactic acid, malic acid, phosphoric acid, potassium acid tartrate, sulfuric acid, and tartaric acid. Alkalies commonly used include: Ammonium bicarbonate, ammonium hydroxide, calcium carbonate, calcium oxide, magnesium carbonate, magnesium hydroxide, magnesium oxide, potassium bicarbonate, potassium carbonate, potassium hydroxide, sodium bicarbonate, sodium carbonate, sodium hydroxide, and sodium sesquicarbonate. Among the buffers and neutralizing agents favored are: Adipic acid, aluminum ammonium sulfate, ammonium phosphate (di- or monobasic), calcium citrate, calcium gluconate, sodium acid pyrophosphate, sodium phosphate (di-, mono-, and tri-basic), sodium pyrophosphate, and succinic acid.

See also **Buffer (Chemical)**; and **pH (Hydrogen Ion Concentration)**.

Functions of Acidulants

In the *baking industry*, acidulants and their salts control pH to inhibit spoilage by microbial actions to enhance the stability of foams (such as whipped egg albumin), to assist in leavening in order to achieve desired volume and flavoring, and to maximize the performance of artificial preservatives. A variety of the food acids previously mentioned is used. For example, citric acid traditionally has been favored by bakers for pie fillings. Baking powders (leavening agents) frequently will contain adipic acid, fumaric acid, and cream of tartar. Fumaric acid, in particular, has been the choice for leavening systems of cakes, pancakes, biscuits, waffles, crackers, cookies, and doughnuts. This acid also provides the desired characteristic flavor for sour rye bread—this eliminating fermentation of the dough to achieve desired flavor. Lactic acid and its salts sometimes are used as dough conditioners.

Acidulants are used in the *soft drink beverage industry* for producing a tart taste, improving flavor balance, modifying the “sweetness” provided by sugar and other sweeteners, extending shelf life by reducing pH value of final product, and improving the performance of antimicrobial agents. Specific acidulants preferred vary with the type of beverage—i.e. carbonated, non-carbonated, dry (reconstituted by addition of water), and low-calorie products.

In the production of *confections and gelatin desserts,* acidulants are used mainly for enhancing flavor, maintaining viscosity, and controlling gel formation. In confections, such as hard candies, acidulants are used to increase tartness and to enhance fruit flavors. Acidulants also contribute to the ease of manufacturing.

In *dairy products,* acidulants, in addition to achieving many of the foregoing functions, also help to process the products. As an example, adipic acid improves the texture and melting characteristics of processed cheese and cheese foods, where pH control is very important.

In *fruit and vegetable processing*, acidulants play somewhat different roles than previously described. These would include reducing process heating requirements through pH control, inactivating certain enzymes that reduce shelf life, and chelation of trace metals that may be present (through catalytic enzymatic oxidation). Citric acid is used widely in canned fruits, such as apricots, peaches, pears, cherries, applesauce, and grapes, to retain the firmness of the products during processing. The acid also provides a desirable tartness in the final products.

In the *processed meat field,* citric acid, along with oxidants, is used to prevent rancidity in frankfurters and sausages. Sodium citrate is used in processing livestock blood, which is used to manufacture some sausages and pet foods.

Acidulants and alkalizers, like other food additives, are controlled by regulatory bodies in most industrial nations. Some of the additives mentioned in this article are considered to be “Generally Regarded as Safe,” having a GRAS classification. These include acetic, adipic, citric, glucone delta lactone, lactic, malic, phosphoric, and tartaric acids. Others are covered by the Code of Federal Registration (FDA) in the United States.

A very orderly and informative article (Dziezak 1990) is suggested as a source of detailed information on this topic.

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ACMITE-AEGERINE. Acmite is a comparatively rare rock-making mineral, usually found in nephelite syenites or other nephelite or leucite-bearing rocks, as phonolites. Chemically, it is a soda-iron silicate, and its name refers to its sharply pointed monoclinic crystals. Bluntly terminated crystals form the variety aegerine, named for Aegir, the Icelandic sea god.

Acmite has a hardness of 6 to 6.5, specific gravity 3.5, vitreous; color brown to greenish-black (aegerine), or red-brown to dark green and black (acmite). Acmite is synonymous with aegerine, but usually restricted to the long slender crystalline variety of brown color.

The original acmite locality is in Greenland. Norway, the former U.S.S.R., Kenya, India, and Mt. St. Hilaire, Quebec, Canada furnish fine specimens. United States localities are Magnet Cove, Arkansas, and Libby, Montana, where a variety carrying vanadium occurs.

ACREE’S REACTION. A test for protein in which a violet ring appears when concentrated sulfuric acid is introduced below a mixture of the unknown solution and a formaldehyde solution containing a trace of ferric oxide.

ACROLEIN AND DERIVATIVES. Acrolein (2-propenal), C_3H_4O, is the simplest unsaturated aldehyde ($CH_2{=}CHCHO$). The primary characteristic of acrolein is its high reactivity due to conjugation of the carbonyl group with a vinyl group. More than 80% of the refined acrolein that is produced today goes into the synthesis of methionine. Much larger quantities of crude acrolein are produced as an intermediate in the production of acrylic acid. More than 85% of the acrylic acid produced worldwide is by the captive oxidation of acrolein.

Acrolein is a highly toxic material with extreme lacrimatory properties. At room temperature acrolein is a liquid with volatility and flammability somewhat similar to acetone; but unlike acetone, its solubility in water is limited. Commercially, acrolein is always stored with hydroquinone and acetic acid as inhibitors. Special care in handling is required because of the flammability, reactivity, and toxicity of acrolein.

The physical and chemical properties of acrolein are given in Table 1.

Economic Aspects

Presently, worldwide refined acrolein nameplate capacity is about 113,000 t/yr. Degussa has announced a capacity expansion in the United States by building a 36,000 t/yr acrolein plant in Theodore, Alabama to support their methionine business. The key producers of refined acrolein are Union Carbide (United States), Degussa (Germany), Atochem (France), and Daicel (Japan).

Reactions and Derivatives

Acrolein is a highly reactive compound because both the double bond and aldehydic moieties participate in a variety of reactions, including oxidation, reduction, reactions with alcohols yielding alkoxy propionaldehydes,

TABLE 1. PROPERTIES OF ACROLEIN

Property	Value
Physical properties	
molecular formula	C_3H_4O
molecular weight	56.06
specific gravity at 20/20°C	0.8427
boiling point, °C at 101.3 kPa[a]	52.69
Chemical properties	
autoignition temperature in air, °C	234
heat of combustion at 25°C, kJ/kg[b]	5383

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert kJ to kcal, divide by 4.184.

acrolein acetals, and alkoxypropionaldehyde acetals, addition of mercaptans yielding 3-methylmercaptopropionaldehyde, reaction with ammonia yielding β-picoline and pyridine, Diels-Alder reactions, and polymerization.

Direct Uses of Acrolein

Because of its antimicrobial activity, acrolein has found use as an agent to control the growth of microbes in process feed lines, thereby controlling the rates of plugging and corrosion.

Acrolein at a concentration of <500 ppm is also used to protect liquid fuels against microorganisms.

W. G. Etzkorn
J. J. Kurland
W. D. Neilsen
Union Carbide Chemicals & Plastics Company Inc.

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ACRYLAMIDE. Acrylamide (NIOSH No. A533250) has been commercially available since the mid-1950s and has shown steady growth since that time, but is still considered a small-volume commodity. Its formula, $H_2{=}CHCONH_2$ (2-propeneamide), indicates a simple chemical, but it is by far the most important member of the series of acrylic and methacrylic amides. Water-soluble polyacrylamides have the most important applications, including potentially large uses in enhanced oil recovery as mobility-control agents in water flooding, additives for oilwell drilling fluids, and aids in fracturing, acidifying, and other operations. Other uses include flocculants for waste-water treatment, the mining industry, and various other process industries, soil stabilization, papermaking aids, and thickeners. Smaller but nonetheless important uses include dye acceptors; polymers for promoting adhesion; additives for textiles, paints, and cement; increasing the softening point and solvent resistance of resins; components of photopolymerizable systems; and cross-linking agents in vinyl polymers.

Physical Properties

The physical properties of solid acrylamide monomer are summarized in Table 1. Typical physical properties of 50% solution in water appear in Table 2.

Chemical Properties

Acrylamide, C_3H_5NO, is an interesting difunctional monomer containing a reactive electron-deficient double bond and an amide group, and it undergoes reactions typical of those two functionalities. It exhibits both weak acidic and basic properties.

TABLE 1. PHYSICAL PROPERTIES OF SOLID ACRYLAMIDE MONOMER

Property	Value
molecular weight	71.08
melting point, °C	84.5 ± 0.3
boiling point, °C at 0.67 kPa[a]	103

[a] To convert kPa to mm Hg, multiply by 7.5.

TABLE 2. PHYSICAL PROPERTIES OF 50% AQUEOUS ACRYLAMIDE SOLUTION

Property	Value
pH	5.0–6.5
refractive index range, 25°C (48–52%)	1.4085–1.4148
viscosity, mPa (= cP) at 25°C	2.71
specific gravity, at 25°C	1.0412
boiling point at 101.3 kPa[a], °C	99–104

[a] To convert kPa to mm Hg, multiply by 7.5.

Manufacture

The current routes to acrylamide are based on the hydration of inexpensive and readily available acrylonitrile (C_3H_3N, 2-propenenitrile, vinyl cyanide, VCN, or cyanoethene) See also **Acrylonitrile**.

Health and Safety Considerations

Contact with acrylamide can be hazardous and should be avoided. The most serious toxicological effect of exposure to acrylamide monomer is as a neurotoxin. In contrast, polymers of acrylamide exhibit very low toxicity.

Economic Aspects

The largest production of acrylamide is in Japan; the United States and Europe also have large production facilities. The principal producers in North America are The Dow Chemical Company, American Cyanamid Company, and Nalco Chemical Company (internal use).

C. E. Habermann
Dow Chemical, USA

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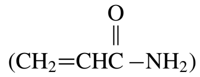
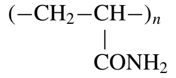
ACRYLAMIDE POLYMERS. Acrylamide,



$$(CH_2{=}CH\overset{\overset{\Large O}{\|}}{C}{-}NH_2)$$

polymerizes in the presence of free-radical initiators to form polyacrylamide chains with the following structure:



$$(-CH_2-\underset{\underset{\textstyle CONH_2}{|}}{CH}-)_n$$

In this article the term *acrylamide polymer* refers to all polymers which contain acrylamide as a major constituent. Consequently, acrylamide polymers include functionalized polymers prepared from polyacrylamide by postreaction and copolymers prepared by polymerizing acrylamide (2-propenamide, C_3N_5NO) with one or more comonomers.

Manufacturing processes have been improved by use of on-line computer control and statistical process control leading to more uniform final products. Production methods now include inverse (water-in-oil) suspension polymerization or polymerization in water on moving belts. Conventional azo, peroxy, redox, and gamma-ray initiators are used in batch and continuous processes.

Physical Properties

Solid Polymer. Completely dry polyacrylamide is a brittle white solid. The physical properties of nonionic polyacrylamide are listed in Table 1.

TABLE 1. PHYSICAL PROPERTIES OF SOLID POLYACRYLAMIDE

Property	Value
density, g/cm^3	1.302
glass-transition temp, °C	188
chain structure	mainly heterotactic linear or branched, some head-to-head addition
crystallinity	amorphous (high mol wt)

Polymers in Solution. Polyacrylamide is soluble in water at all concentrations, temperatures, and pH values.

In general nonionic polyacrylamides do not interact strongly with neutral inorganic salts.

Flow Properties. In water, high molecular weight polyacrylamide forms viscous homogeneous solutions.

Chemical Properties

The preparation of polyacrylamides and postpolymerization reactions on polyacrylamides are usually conducted in water. Reactions on the amide groups of polyacrylamides are often more complicated than reactions of simple amides because of neighboring groups' effects.

Post-reactions of polyacrylamide to introduce anionic, cationic, or other functional groups are often attractive from a cost standpoint. This approach can suffer, however, from side reactions resulting in cross-linking or the introduction of unwanted functionality. Reactions include hydrolysis, sulfomethylation, methylol formation, reaction with other aldehydes, transamidation, Hoffman degradation, and reaction with chlorine.

Uses

Polyacrylamides are classified according to weight-average molecular weight ($\overline{m}_w$) as follows: high 15×10^6; low 2×10^5; and very low 2×10^3.

Most uses for high molecular weight polyacrylamides in water treating, mineral processing, and paper manufacture are based on the ability of these polymers to flocculate small suspended particles by charge neutralization and bridging. Low molecular weight polymers are employed as dispersants, crystal growth modifiers, or selective mineral depressants. In oil recovery, polyacrylamides adjust the rheology of injected water so that the polymer solution moves uniformly through the rock pores, sweeping the oil ahead of it. Other applications such as superabsorbents and soil modification rely on the very hydrophilic character of polyacrylamides.

Suppliers of polyacrylamide are listed in Table 2.

Safety and Health

Dry nonionic and cationic material caused no skin and minimal eye irritation during primary irritation studies with rabbits. Dry anionic polyacrylamide did not produce any eye or skin irritation in laboratory animals. Emulsion nonionic polyacrylamide produced severe eye irritation in rabbits, while anionic and cationic material produced minimal eye irritation in rabbits. Polyacrylamides are used safely for numerous indirect food packaging applications, potable water, and direct food applications.

JOSEPH KOZAKIEWICZ
DAVID LIPP
American Cyanamid Company

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ACRYLATES AND METHACRYLATES. A wide range of plastic materials that date back to the pioneering work of Redtenbacher before 1850, who prepared acrylic acid by oxidizing acrolein

$$\mathrm{CH_2{=}CHCHO} \xrightarrow{\mathrm{O}} \mathrm{CH_2{=}CHCOOH}.$$

At a considerably later date, Frankland prepared ethyl methacrylate and methacrylic acid from ethyl-α-hydroxyisobutyrate and phosphorus trichloride. Tollen prepared acrylate esters from 2,3-dibromopropionate esters and zinc. Otto Rohm, in 1901, described the structures of the liquid condensation products (including dimers and trimers) obtained from the action of sodium alkoxides on methyl and ethyl acrylate. Shortly after World War I, Rohm introduced a new acrylate synthesis, noting that an acrylate is formed in good yield from heating ethylene cyanohydrin and sulfuric acid and alcohol. A major incentive for the development of a clear, tough plastic acrylate was in connection with the manufacture of safety glass.

TABLE 2. SUPPLIERS OF POLYACRYLAMIDE

Region	Companies
United States	Allied Colloids, Inc.
	American Cyanamid Co.
	Aqua Ben Corp.
	Betz Laboratories, Inc.
	Calgon Corp. (Merck & Co.)
	Chemtall, Inc. (SNF Floerger)
	Dearborn Chemical Co. (W. R. Grace & Co.)
	The Dow Chemical Company
	Drew Chemical Corporation (Ashland Chemical, Inc.)
	Exxon Chemical Co.
	Hercules, Inc.
	Nalco Chemical Co.
	Polypure, Inc.
	Secodyne, Inc.
	Stockhausen, Inc.
Europe	Allied Colloids, Ltd.
	American Cyanamid Co.
	BASF AG
	Chemische Fabrik Stockhausen & Cie
	The Dow Chemical Company
	SNF Floerger (France)
	Kemira Oy (Finland)
	Rohm GmbH
	Rhône-Poulenc Specialties Chimiques (France)
Japan	Dai-Ichi Kogyo Seiyaku Co., Ltd.
	Kurita Water Industries, Ltd.
	Kyoritsu Yuki Co., Ltd.
	Mitsubishi Chemical Industries, Ltd.
	Mitsui-Cyanamid, Ltd.
	Sankyo Kasei Co., Ltd.
	Sanyo Chemical Industries, Ltd.
	Takenaka Komuten Co., Ltd.
	Toa Gosei Chemical Industry Co., Ltd.

Ethyl methacrylate went into commercial production as early as 1933. The synthesis proceeded in the following steps:

(1) Acetone and hydrogen cyanide, generated from sodium cyanide and acid, gave acetone cyanohydrin

$$\mathrm{HCN + CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CN}$$

(2) The acetone cyanohydrin was converted to ethyl α-hydroxyisobutyrate by reaction with ethyl alcohol and dilute sulfuric acid

$$\mathrm{(CH_3)_2C(OH)CN + C_2H_5OH \xrightarrow{H_2SO_4} (CH_3)_2C(OH)COOC_2H_5}$$

(3) The hydroxy ester was dehydrated with phosphorus pentoxide to produce ethyl methacrylate

$$\mathrm{(CH_3)_2C(OH)COOC_2H_5 \xrightarrow{P_2O_5} CH_2{=}C(CH_3)COOC_2H_5}$$

In 1936, the methyl ester of methacrylic acid was introduced and used to produce an "organic glass" by cast polymerization. Methyl methacrylate was made initially through methyl α-hydroxyisobutyrate by the same process previously indicated for the ethyl ester. Over the years, numerous process changes have occurred and costs lowered, making these plastics available on a high production basis for many hundreds of uses. For example, the hydrogen cyanide required is now produced catalytically from natural gas, ammonia, and air.

As with most synthetic plastic materials, they commence with the monomers. Any of the common processes, including bulk, solution, emulsion, or suspension systems may be used in the free-radical polymerization or copolymerization of acrylic monomers. The molecular weight and physical properties of the products may be varied over a wide range by proper selection of acrylic monomer and monomer mixes, type of process, and process conditions.

In bulk polymerization, no solvents are employed and the monomer acts as the solvent and continuous phase in which the process is carried out. Commercial bulk processes for acrylic polymers are used mainly in the production of sheets, rods and tubes. Bulk processes are also used on a much smaller scale in the preparation of dentures and novelty items and in the preservation of biological specimens. Acrylic castings are produced by pouring monomers or partially polymerized sirups into suitably designed molds and completing the polymerization. Acrylic bulk polymers consist essentially of poly(methyl methacrylate) or copolymers with methyl methacrylate as the major component. Free radical initiators soluble in the monomer, such as benzoyl peroxide, are the catalysts for the polymerization. Aromatic tertiary amines, such as dimethylaniline, may be used as accelerators in conjunction with the peroxide to permit curing at room temperature. However, colorless products cannot be obtained with amine accelerators because of the formation of red or yellow colors. As the polymerization proceeds, a considerable reduction in volume occurs which must be taken into consideration in the design of molds. At 25°C, the shrinkage of methyl methacrylate in the formation of the homopolymer is 21%.

Solutions of acrylic polymers and copolymers find wide use as thermoplastic coatings and impregnating fluids, adhesives, laminating materials, and cements. Solutions of interpolymers convertible to thermosetting compositions can also be prepared by inclusion of monomers bearing reactive functional groups which are capable of further reaction with appropriate crosslinking agents to give three-dimensional polymer networks. These polymer systems may be used in automotive coatings and appliance enamels, and as binders for paper, textiles, and glass or nonwoven fabrics. Despite the relatively low molecular weight of the polymers obtained in solution, such products are often the most appropriate for the foregoing uses. Solution polymerization of acrylic esters is usually carried out in large stainless steel, nickel, or glass-lined cylindrical kettles, designed to withstand at least 50 psig. The usual reaction mixture is a 40–60% solution of the monomers in solvent. Acrylic polymers are soluble in aromatic hydrocarbons and chlorohydrocarbons.

Acrylic emulsion polymers and copolymers have found wide acceptance in many fields, including sizes, finishes and binders for textiles, coatings and impregnants for paper and leather, thermoplastic and thermosetting protective coatings, floor finishing materials, adhesives, high-impact plastics, elastomers for gaskets, and impregnants for asphalt and concrete.

Advantages of emulsion polymerization are rapidity and production of high-molecular-weight polymers in a system of relatively low viscosity. Difficulties in agitation, heat transfer, and transfer of materials are minimized. The handling of hazardous solvents is eliminated. The two principal variations in technique used for emulsion polymerization are the redox and the reflux methods.

Suspension polymerization also is used. When acrylic monomers or their mixtures with other monomers are polymerized while suspended (usually in aqueous system), the polymeric product is obtained in the form of small beads, sometimes called pearls or granules. Bead polymers are the basis of the production of molding powders and denture materials. Polymers derived from acrylic or methacrylic acid furnish exchange resins of the carboxylic acid type. Solutions in organic solvents furnish lacquers, coatings and cements, while water-soluble hydrolysates are used as thickeners, adhesives, and sizes.

The basic difference between suspension and emulsion processes lies in the site of the polymerization, since initiators insoluble in water are used in the suspension process. Suspensions are produced by vigorous and continuous agitation of the monomer and solvent phases. The size of the drop will be determined by the rate of agitation, the interfacial tension, and the presence of impurities and minor constituents of the recipe. If agitation is stopped, the droplets coalesce into a monomer layer. The water serves as a dispersion medium and heat-transfer agent to remove the heat of polymerization. The process and resulting product can be influenced by the addition of colloidal suspending agents, thickeners, and salts.

Product Groupings. The principal acrylic plastics are cast sheet, molding powder, and high-impact molding powder. The cast acrylic sheet is formable, transparent, stable, and strong. Representative uses include architectural panels, aircraft glazing, skylights, lighted outdoor signs, models, product prototypes, and novelties. Molding powders are used in the mass production of numerous intricate shapes, such as automotive lights, lighting fixture lenses, and instrument dials and control panels for autos, aircraft, and appliances. The high-impact acrylic molding powder yields a somewhat less transparent product, but possesses unusual toughness for such applications as toys, business machine components, blow-molded bottles, and outboard motor shrouds. The various acrylic resins find numerous uses, with varied and wide use in coatings. Acrylic latexes are composed mainly of monomers of the acrylic family, such as methyl methacrylate, butyl methacrylate, methyl acrylate, and 2-ethylhexylacrylate. Additional monomers, such as styrene or acrylonitrile, can be polymerized with acrylic monomers. Acrylic latexes vary considerably in their properties, mainly affected by the monomers used, the particle size, and the surfactant system of the latex. Generally, acrylic latexes are cured by loss of water only, do not yellow, possess a good exterior durability, are tough, and usually have good abrasion resistance. The acrylic polymers are reasonably costly and some latexes do not have very good color compatibility. Acrylic latex paints can be used for concrete floors, interior flat and semigloss finishes, and exterior surfaces.

ACRYLIC ACID AND DERIVATIVES. [CAS: 79-10-7]. Acrylic acid (propenoic acid) was first prepared in 1847 by air oxidation of acrolein. Interestingly, after use of several other routes over the past half century, it is this route, using acrolein from the catalytic oxidation of propylene, that is currently the most favored industrial process.

Acrylates are primarily used to prepare emulsion and solution polymers. The emulsion polymerization process provides high yields of polymers in a form suitable for a variety of applications. Acrylate emulsions are used in the preparation of both interior and exterior paints, floor polishes, and adhesives. Solution polymers of acrylates, frequently with minor concentrations of other monomers, are employed in the preparation of industrial coatings. Polymers of acrylic acid can be used as superabsorbents in disposable diapers, as well as in formulation of superior, reduced-phosphate-level detergents.

The polymeric products can be made to vary widely in physical properties through controlled variation in the ratios of monomers employed in their preparation, cross-linking, and control of molecular weight. They share common qualities of high resistance to chemical and environmental attack, excellent clarity, and attractive strength properties.

Physical Properties

Physical properties of acrylic acid and representative derivatives appear in Table 1.

Reactions

Acrylic acid and its esters may be viewed as derivatives of ethylene, in which one of the hydrogen atoms has been replaced by a carboxyl or carboalkoxyl group. This functional group may display electron-withdrawing ability through inductive effects of the electron-deficient carbonyl carbon atom, and electron-releasing effects by resonance involving the electrons of the carbon–oxygen double bond. Therefore, these compounds react readily with electrophilic, free-radical, and nucleophilic agents.

Specialty Acrylic Esters

Higher alkyl acrylates and alkyl-functional esters are important in copolymer products, in conventional emulsion applications for coatings and adhesives, and as reactants in radiation-cured coatings and inks. In general, they are produced in direct or transesterification batch processes because of their relatively low volume.

Health and Safety Factors

The toxicity of common acrylic monomers has been characterized in animal studies using a variety of exposure routes. Toxicity varies with level, frequency, duration, and route of exposure. The simple higher esters of acrylic acid are usually less absorbed and less toxic than lower esters. In general, acrylates are more toxic than methacrylates.

TABLE 1. PHYSICAL PROPERTIES OF ACRYLIC ACID DERIVATIVES

Property	Acrylic acid	Acrolein	Acrylic anhydride	Acryloyl chloride	Acrylamide
molecular formula	$C_3H_4O_2$	C_3H_4O	$C_6H_6O_3$	C_3H_3OCl	C_3H_5ON
melting point, °C	13.5	−88			84.5
boiling point[a], °C	141	52.5	38[b]	75	125[c]
refractive index[d], n_D	1.4185[e]	1.4017	1.4487	1.4337	

[a] At 101.3 kPa = 1 atm unless otherwise noted.

[b] At 0.27 kPa.

[c] At 16.6 kPa.

[d] At 20°C, unless otherwise noted.

[e] At 25°C.

Current TLV/TWA values are provided in Material Safety Data Sheets provided by manufacturers on request.

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Additional Reading

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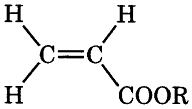
Hydrocarbon Process. **60**(11), 124 (1981).

Snyder, T.P. and C.G. Hill, Jr., *Catal. Rev. Sci. Eng.* **31**, 43–95 (1989).

ACRYLIC ESTER POLYMERS. Acrylic esters are represented by the generic formula



The nature of the R group determines the properties of each ester and the polymers it forms. Polymers of this class are amorphous and are distinguished by their water-clear color and their stability on aging. Acrylic monomers are extremely versatile building blocks. They are relatively moderate to high boiling liquids that readily polymerize or copolymerize with a variety of other monomers. Copolymers with methacrylates, vinyl acetate, styrene, and acrylonitrile are commercially significant. Polymers designed to fit specific application requirements ranging from soft, tacky adhesives to hard plastics can be tailored from these versatile monomers. Although the acrylics have been higher in cost than many other common monomers, they find use in high quality products where their unique characteristics and efficiency offset the higher cost.

Physical Properties

To a large extent, the properties of acrylic ester polymers (Table 1) depend on the nature of the alcohol radical and the molecular weight of the polymer. As is typical of polymeric systems, the mechanical properties of acrylic polymers improve as molecular weight is increased; however, beyond a critical molecular weight, which often is about 100,000 to 200,000 for amorphous polymers, the improvement is slight and levels off asymptotically.

Chemical Properties

Under conditions of extreme acidity or alkalinity, acrylic ester polymers can be made to hydrolyze to poly(acrylic acid) or an acid salt and the corresponding alcohol. However, acrylic polymers and copolymers have a greater resistance to both acidic and alkaline hydrolysis than competitive poly(vinyl acetate) and vinyl acetate copolymers.

Acrylic polymers are fairly insensitive to normal uv degradation since the primary uv absorption of acrylics occurs below the solar spectrum.

TABLE 1. PHYSICAL PROPERTIES OF ACRYLIC POLYMERS

Polymer[a]	Monomer molecular formula	T_g, °C
methyl acrylate	$C_4H_6O_2$	6
ethyl acrylate	$C_5H_8O_2$	−24
propyl acrylate	$C_6H_{10}O_2$	−45
isopropyl acrylate	$C_6H_{10}O_2$	−3
n-butyl acrylate	$C_7H_{12}O_2$	−50
sec-butyl acrylate	$C_7H_{12}O_2$	−20
isobutyl acrylate	$C_7H_{12}O_2$	−43
tert-butyl acrylate	$C_7H_{12}O_2$	43
hexyl acrylate	$C_9H_{16}O_2$	−57
heptyl acrylate	$C_{10}H_{18}O_2$	−60
2-heptyl acrylate	$C_{10}H_{18}O_2$	−38
2-ethylhexyl acrylate	$C_{11}H_{20}O_2$	−65
2-ethylbutyl acrylate	$C_9H_{16}O_2$	−50
dodecyl acrylate	$C_{15}H_{28}O_2$	−30
hexadecyl acrylate	$C_{19}H_{36}O_2$	35
2-ethoxyethyl acrylate	$C_7H_{12}O_3$	−50
isobornyl acrylate	$C_{13}H_{20}O_2$	94
cyclohexyl acrylate	$C_9H_{14}O_2$	16

[a] Density (glcm^3) and refractive index (n_D) for methyl acrylate, ethyl acrylate, and *n*-butyl acrylate: 1.22, 1.479; 1.12, 1.464; 1.08, 1.474. Density for isopropyl acrylate = 1.08 g/cm^3.

TABLE 2. PHYSICAL PROPERTIES OF ACRYLIC MONOMERS

Acrylate	Molecular weight	bp, °C[a]	d^{25}, g/cm^3
methyl	86	79–81	0.950
ethyl	100	99–100	0.917
n-butyl	128	144–149	0.894
isobutyl	128	61–63[b]	0.884
t-butyl	128	120	0.879
2-ethylhexyl	184	214–220	0.880

[a] At 101.3 kPa unless otherwise noted.

[b] At 6.7 kPa = 50 mm Hg.

Acrylic Ester Monomers

Some of the physical properties of the principal commercial acrylic esters are given in Table 2.

There are currently two principal processes used for the manufacture of monomeric acrylic esters: the semicatalytic Reppe process and the propylene oxidation process. The newer propylene oxidation process is preferred because of economy and safety.

The toxicities of acrylic monomers range from moderate to slight. In general, they can be handled safely and without difficulty by trained personnel following established safety practices.

Radical Polymerization

Usually, free-radical initiators such as azo compounds or peroxides are used to initiate the polymerization of acrylic monomers. Photochemical and radiation-initiated polymerizations are also well known. Methods of radical polymerization include bulk, solution, emulsion, suspension, graft copolymerization, radiation-induced, and ionic with emulsion being the most important.

The free-radical polymerization of acrylic monomers follows a classical chain mechanism in which the chain-propagation step entails the head-to-tail growth of the polymeric free radical by attack on the double bond of the monomer.

The vast majority of all commercially prepared acrylic polymers are copolymers of an acrylic ester monomer with one or more different monomers. Copolymerization greatly increases the range of available polymer properties and has led to the development of many different resins suitable for a broad variety of applications.

In general, acrylic ester monomers copolymerize readily with each other or with most other types of vinyl monomers by free-radical processes.

Health and Safety Factors

Acrylic polymers are considered to be nontoxic. In fact, the FDA allows certain acrylate polymers to be used in the packaging and handling of food.

Potential health and safety problems of acrylic polymers occur in their manufacture. During manufacture, considerable care is exercised to reduce the potential for violent polymerizations and to reduce exposure to flammable and potentially toxic monomers and solvents.

Uses

Acrylic ester polymers are used primarily in coatings, textiles, adhesives, and paper.

2-Cyanoacrylic Ester Polymers

The polymers of the 2-cyanoacrylic esters, more commonly known as the alkyl 2-cyanoacrylates, are hard glassy resins that exhibit excellent adhesion to a wide variety of materials. The polymers are spontaneously formed when their liquid precursors or monomers are placed between two closely fitting surfaces. The spontaneous polymerization of these very reactive liquids and the excellent adhesion properties of the cured resins combine to make these compounds a unique class of single-component, ambient-temperature-curing adhesive of great versatility (Table 3). The materials that can be bonded run the gamut from metals, plastics, most elastomers, fabrics, and woods to many ceramics.

The utility of these adhesives arises from the electron-withdrawing character of the groups adjacent to the polymerizable double bond, which accounts for both the extremely high reactivity or cure rate and their polar nature, which enables the polymers to adhere tenaciously to many diverse substrates.

At present, a number of manufacturers in the United States, Europe, Japan, and elsewhere marked extended lines of these adhesives all over the

TABLE 3. ADHESIVE BOND PROPERTIES OF 2-CYANOACRYLIC ESTERS WITH METALS AND VARIOUS POLYMERIC MATERIALS

	Ester type					
Property	Methyl	Ethyl[a]	Butyl	Isobutyl	Methoxyethyl	Ethoxyethyl
			SET TIME, s			
steel	20	10	30	20	15	5
nitrile rubber	5	3	5	5	5	3
ABS	20	10	20	20	5	5
polycarbonate	20	10	20	20	60	20
PVC	5	3	2	5		10
phenolic resin	5	3	30	5	25	5
			BOND STRENGTH, kPa[b]			
steel	206	172	151	96	206	165
ABS	48	48	96	48	48	48
polycarbonate	69	69	90	69		41
PVC	96	96	62	83	55	69
phenolic resin	69	76	90	62	62	55

[a] Set times for allyl esters are similar to those for ethyl esters, as are bond strengths to steel, ABS, and PC.

[b] To convert kPa to psi multiply by 0.145.

world. Some of the major producers and their trademarks include Loctite (Prism and Superbonder), Toagosei (Aron Alpha, Krazy Glue), Henkel (Sicomet), National Starch (Permabond), Sumitomo (Cyanonond), Three Bond (Super Three), and Alpha Giken (Alpha Ace, Alpha Techno).

Manufacture and Processing. The cyanoacrylic esters are prepared via the Knoevenagel condensation reaction, in which the corresponding alkyl cyanoacetate reacts with formaldehyde in the presence of a basic catalyst to form a low molecular weight polymer. The polymer slurry is acidified and the water is removed. Subsequently, the polymer is cracked and redistilled at a high temperature onto a suitable stabilizer combination to prevent premature repolymerization. Strong protonic or Lewis acids are normally used in combination with small amounts of a free-radical stabilizer.

Adhesives formulated from the 2-cyanoacrylic esters typically contain stabilizers and thickeners, and may also contain tougheners, colorants, and other special property-enhancing additives.

Economic Aspects. Production of the 2-cyanoacrylic ester adhesives on a worldwide basis is estimated to be approximately 2400 metric tons. This amounts to only 0.02% of the total volume of adhesive produced but about 3% of the dollar volume.

Because of the high costs of raw materials and the relatively complex synthesis, the 2-cyanoacrylic esters are moderately expensive materials when considered in bulk quantities. In typical bonding applications, where single drops are adequate for bonding, the adhesives are very economical to use.

Health and Safety Factors. The 2-cyanoacrylic esters have sharp, pungent odors and are lacrimators, even at very low concentrations. The TLV for methyl 2-cyanoacrylate is 2 ppm and the short-term exposure limit is 4 ppm. Good ventilation when using the adhesives is essential.

Eye and skin contact should be avoided because of the adhesive's rapid tissue-bonding capabilities.

Both the liquid and cured 2-cyanoacrylic esters support combustion.

Uses. Some of the market segments served by these versatile materials include automative, electronic, sporting goods, toys, hardware, morticians, law enforcement, cosmetics, jewelry, and medical devices. Although they are not approved for such use in the United States, their strong tissue bonding characteristics have led to their use as chemical sutures and hemostatic agents in other countries around the world.

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ACRYLIC PAINT. See **Paint and Finish Removers**.

ACRYLIC PLASTICS. A wide range of plastic materials dates back to the pioneering work of Redtenbacher before 1850 who prepared acrylic acid by oxidizing acrolein

$$CH = CHCHO \xrightarrow{O} CH_2{=}CHCOOH$$

At a considerably later date, Frankland prepared ethyl methacrylate and methacrylic acid from ethyl α-hydroxyisobutyrate and phosphorus trichloride. Tollen prepared acrylate esters from 2,3-dibromopropionate esters and zinc. Otto Rohm, in 1901, described the structures of the liquid condensation products (including dimers and trimers) obtained from the action of sodium alkoxides on methyl and ethyl acrylate. Shortly after World War I, Rohm introduced a new acrylate synthesis, noting that an acrylate is formed in good yield from heating ethylene cyanohydrin and sulfuric acid and alcohol. A major incentive for the development of a clear, tough plastic acrylate was for use in the manufacture of safety glass.

Ethyl methacrylate went into commercial production in 1933. The synthesis proceeded in the following steps:

(1) Acetone and hydrogen cyanide, generated from sodium cyanide and acid, gave acetone cyanohydrin

$$HCN + CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CN$$

(2) The acetone cyanohydrin was converted to ethyl α-hydroxyiso butyrate by reaction with ethyl alcohol and dilute sulfuric acid

$$(CH_3)_2C(OH)CN + C_2H_5OH \xrightarrow{H_2SO_4} (CH_3)_2C(OH)COOC_2H_5$$

(3) The hydroxy ester was dehydrated with phosphorus pentoxide to produce ethyl methacrylate

$$(CH_3)_2C(OH)COOC_2H_5 \xrightarrow{P_2O_5} CH_2{=}C(CH_3)COOC_2H_5$$

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A developing and potentially large volume use for acrylics is in the video, audio, and data-storage disk markets. The properties, as well as ease of fabrication, have made acrylics a primary choice for these applications.

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http://www.4spe.org/ Society of Plastics Engineers.

ACRYLONITRILE. [CAS: 107-13-1]. Today over 90% of the approximately 4,000,000 metric tons of acrylonitrile (also called acrylic acid nitrile, propylene nitrile, vinyl cyanide, and propenoic acid nitrile) produced worldwide each year use the Sohio-developed ammoxidation process. Acrylonitrile is among the top 50 chemicals produced in the United States as a result of the tremendous growth in its use as a starting material for a wide range of chemical and polymer products. Acrylic fibers remain the largest use of acrylonitrile; other significant uses are in resins and nitrile elastomers and as an intermediate in the production of adiponitrile and acrylamide.

Physical Properties

Acrylonitrile (C_3H_3N, mol wt = 53.064) is an unsaturated molecule having a carbon–carbon double bond conjugated with a nitrile group. It is a polar molecule because of the presence of the nitrogen heteroatom. Tables 1 and 2 list some physical properties and thermodynamic information, respectively, for acrylonitrile.

Acrylonitrile is miscible in a wide range of organic solvents, including acetone, benzene, carbon tetrachloride, diethyl ether, ethyl acetate, ethylene cyanohydrin, petroleum ether, toluene, some kerosenes, and methanol.

Acrylonitrile has been characterized using infrared, Raman, and ultraviolet spectroscopies, electron diffraction, and mass spectroscopy.

Chemical Properties

Acrylonitrile undergoes a wide range of reactions at its two chemically active sites, the nitrile group and the carbon–carbon double bond. Detailed descriptions of specific reactions have been given.

Manufacturing and Processing

Acrylonitrile is produced in commercial quantities almost exclusively by the vapor-phase catalytic propylene ammoxidation process developed by Sohio.

$$C_3H_6 + NH_3 + \tfrac{3}{2}O_2 \xrightarrow{\text{catalyst}} C_3H_3N + 3H_2O$$

Economic Aspects

More than half of the worldwide acrylonitrile production is situated in Western Europe and the United States. In the United States, production is dominated by BP Chemicals, with more than a third of the domestic capacity. The export market has been an increasingly important outlet for U.S. production, exports growing from around 10% in the mid-1970s to 53% in 1987 and 43% in 1988.

TABLE 1. PHYSICAL PROPERTIES OF ACRYLONITRILE

Property	Value
appearance/odor	clear, colorless liquid with faintly pungent odor
boiling point, °C	77.3
freezing point, °C	−83.5
density, 20°C, g/cm^3	0.806
vapor density (air = 1)	1.8
pH (5% aqueous solution)	6.0–7.5
viscosity, 25°C, mPa · s(= cP)	0.34

TABLE 2. THERMODYNAMIC DATA[a]

Property	Value
flash point, °C	0
autoignition temperature, °C	481
heat of combustion, liquid, 25°C, kJ/mol	1761.5
heat of vaporization, 25°C, kJ/mol	32.65

[a] To convert kJ to kcal, divide by 4.184.

Storage and Transport

Acrylonitrile is transported by rail car, barge, and pipeline. Department of Transportation (DOT) regulations require labeling acrylonitrile as a flammable liquid and poison.

Health and Safety Factors

Acrylonitrile is highly toxic if ingested, with an acute LDL_0 value for laboratory rats of 113 mg/kg. It is moderately toxic if inhaled (rat $LCL_0 =$ 500 ppm/4 h), and it is extremely irritating and corrosive to skin and eyes. Acrylonitrile is categorized as a cancer hazard by OSHA.

Acrylonitrile will polymerize violently in the absence of oxygen if initiated by heat, light, pressure, peroxide, or strong acids and bases. It is combustible and ignites readily, producing toxic combustion products such as hydrogen cyanide, nitrogen oxides, and carbon monoxide.

Federal regulations (40 CFR 261) classify acrylonitrile as a hazardous waste, and it is listed as Hazardous Waste Number U009. Disposal must be in accordance with federal (40 CFR 262, 263, 264), state, and local regulations only at properly permitted facilities.

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ACRYLONITRILE POLYMERS

SAN

Acrylonitrile has found its way into a great variety of polymeric compositions based on its polar nature and reactivity. Some of these areas include adhesives and binders, antioxidants, medicines, dyes, electrical insulations, emulsifying agents, graphic arts materials, insecticides, leather, paper, plasticizers, soil-modifying agents, solvents, surface coatings, textile treatments, viscosity modifiers, azeotropic distillations, artificial organs, lubricants, asphalt additives, water-soluble polymers, hollow spheres, crosslinking agents, and catalyst treatments.

SAN Physical Properties and Test Methods

Styrene–acrylonitrile (SAN) resins possess many physical properties desired for thermoplastic applications. They are characteristically hard, rigid, and dimensionally stable with load bearing capabilities. They are also transparent, have high heat distortion temperatures, possess excellent gloss and chemical resistance, and adapt easily to conventional thermoplastic fabrication techniques.

TABLE 1. PROPERTIES OF INJECTION-MOLDED COMMERCIAL SAN RESINS[a]

Property	Monsanto Lustran-35	Dow Tyril-880
tensile strength, MPa[b]	79.4	82.1
ultimate elongation, %	3.0	3.0
Izod impact strength, J/m[c]	24.0	26.7
hardness—Rockwell M	83	80
coefficient of linear thermal expansion, cm/(cm·°C)	6.8×10^{-5}	6.6×10^{-5}
flammability, cm/min		2.0
specific heat, J/(g·K)[d]		1.3
dielectric constant, kHz (MHz)		3.18 (3.02)
water absorption, % in 24 h	0.25	0.35
specific gravity	1.07	1.08

[a] Data taken from Monsanto and Dow product data sheets.

[b] To convert MPa to psi multiply by 145.

[c] To convert J/m to ftlb/in. divide by 53.39.

[d] To convert J to cal divide by 4.184.

SAN polymers are random linear amorphous copolymers. Physical properties are dependent on molecular weight and the percentage of acrylonitrile. An increase of either generally improves physical properties, but may cause a loss of processibility or an increase in yellowness. Various processing aids and modifiers can be used to achieve a specific set of properties. Modifiers may include mold release agents, uv stabilizers, antistatic aids, elastomers, flow and processing aids, and reinforcing agents such as fillers and fibers. Some typical physical properties are listed in Table 1.

SAN Chemical Properties and Analytical Methods

SAN resins show considerable resistance to solvents and are insoluble in carbon tetrachloride, ethyl alcohol, gasoline, and hydrocarbon solvents. They are swelled by solvents such as benzene, ether, and toluene. Polar solvents such as acetone, chloroform, dioxane, methyl ethyl ketone, and pyridine will dissolve SAN.

The properties of SAN are significantly altered by water absorption. The equilibrium water content increases with temperature while the time required decreases. A large decrease in T_g can result. Strong aqueous bases can degrade SAN by hydrolysis of the nitrile groups.

SAN Manufacture

Commercially, SAN is manufactured by three processes: emulsion, suspension, and continuous bulk.

Processing. SAN copolymers may be processed using the conventional fabrication methods of extrusion, blow molding, injection molding, thermoforming, and casting.

Other Copolymers

Acrylonitrile copolymerizes readily with many electron-donor monomers other than styrene. Hundreds of acrylonitrile copolymers have been reported, and a comprehensive listing of reactivity ratios for acrylonitrile copolymerizations is readily available.

Copolymers of acrylonitrile and methyl acrylate and terpolymers of acrylonitrile, styrene, and methyl methacrylate are used as barrier polymers. Acrylonitrile copolymers and multipolymers containing butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, hydroxyethyl acrylate, methyl methacrylate, vinyl acetate, vinyl ethers, and vinylidene chloride are also used in barrier films, laminates, and coatings. Environmentally degradable polymers useful in packaging are prepared from polymerization of acrylonitrile with styrene and methyl vinyl ketone.

Economic Aspects

Since its introduction in the 1950s, SAN has shown steady growth. The combined properties of SAN copolymers such as optical clarity, rigidity, chemical and heat resistance, high tensile strength, and flexible molding characteristics, along with reasonable price have secured their market position. The largest portion of SAN (80%) is incorporated into ABS resins, and their markets are inexorably joined.

There are two major producers of SAN resin in the United States, Monsanto Chemical Company and The Dow Chemical Company, which market these materials under the names of Lustran and Tyril, respectively.

Health and Toxicology

SAN resins themselves appear to pose few health problems in that they have been approved by the FDA for food packaging use. The main concern is that of toxic residuals, e.g., acrylonitrile, styrene, or other polymerization components such as emulsifiers, stabilizers, or solvents. Each component must be treated individually for toxic effects and safe exposure level.

ABS Resins

Acrylonitrile–butadiene–styrene (ABS) polymers are composed of elastomer dispersed as a grafted particulate phase in a thermoplastic matrix of styrene and acrylonitrile copolymer (SAN). The presence of SAN grafted onto the elastomeric component, usually polybutadiene or a butadiene copolymer, compatabilizes the rubber with the SAN component. Property advantages provided by this graft terpolymer include excellent toughness, good dimensional stability, good processibility, and chemical resistance. Property balances are controlled and optimized by adjusting elastomer particle size, morphology, microstructure, graft structure, and SAN composition and molecular weight. Therefore, although the polymer is a relatively low cost engineering thermoplastic the system is structurally complex. This complexity is advantageous in that altering these structural and compositional parameters allows considerable versatility in the tailoring of properties to meet specific product requirements. This versatility may be even further enhanced by adding various monomers to raise the heat deflection temperature, impart transparency, confer flame retardancy, and, through alloying with other polymers, obtain special product features. Consequently, research and development in ABS systems is active and continues to offer promise for achieving new product opportunities.

Physical Properties. The range of properties typically available for general purpose ABS is illustrated in Table 2. Numerous grades of ABS are available including new alloys and specialty grades for high heat, plating, flaming-retardant, or static dissipative product requirements.

Chemical Properties. The behavior of ABS may be inferred from consideration of the functional groups present within the polymer.

Chemical Resistance. The polar character of the nitrile group reduces interration of the polymer with hydrocarbon solvents, mineral and vegetable oils, waxes, and related household and commercial materials. Good chemical resisatance provided by the presence of acrylonitrile as a comonomer combined with the relatively low water absorptivity ($<1\%$) results in high resistance to the staining agents typically encountered in household applications.

Processing Stability. As with elastomers or other rubber modified polymers, the presence of double bonds in the elastomeric phase increases sensitivity to thermal oxidation either during processing or end use. Antioxidants are generally added at the compounding step to ensure retention of physical properties. Physical effects can also have marked effects on mechanical properties due to orientation, molded-in stress, and the agglomeration of dispersed rubber particles under very severe conditions. Proper drying conditions are essential to prevent moisture-induced splay. Discoloration can be minimized by reducing stock temperature during molding or extrusion.

Thermal Oxidative Stability. ABS undergoes autoxidation with the polybutadiene component more sensitive to thermal oxidation than the styrene–acrylonitrile component. Antioxidants substantially improve oxidative stability. Studies on the oven aging of molded parts have shown that oxidation is limited to the outer surface (<0.2 mm), i.e., the oxidation process is diffusion limited.

Photoxidative Stability. Unsaturation present as a structural feature in the polybutadiene component of ABS (also in high impact polystyrene, rubber-modified PVC, and butadiene-containing elastomers) also increases lability with regard to photooxidative degradation. Such degradation also only occurs in the outermost layer, and impact loss upon irradiation can be attributed to embrittlement of the rubber and possibly to scission of the grafted styrene–acrylonitrile copolymer. Applications involving extended outdoor exposure, especially in direct sunlight, require protective measures such as the use of stabilizing additives, pigments, and protective coatings and film.

Flammability. The general-purpose grades are usually recognized as 94 HB according to the requirements of Underwriters' Laboratories UL94 and also meet the requirements, dependent on thickness, of the Motor Vehicle Safety Standard 302.

Polymerization. In all manufacturing processes, grafting is achieved by the free-radical copolymerization of styrene and acrylonitrile monomers in the presence of an elastomer. Ungrafted styrene–acrylonitrile copolymer is formed during graft polymerization or added afterward.

Manufacturing. There are three commercial processes for manufacturing ABS: emulsion, mass, and mass-suspension. ABS is sold as an unpigmented product for on-line coloring using color concentrates during molding, or as precolored pellets matched to exacting requirements.

Analysis. Analytical investigations may be undertaken to identify the presence of an ABS polymer, characterize the polymer, or identify nonpolymeric ingredients. Fourier transfrom infrared (ftir) spectroscopy is the method of choice to identify the presence of an ABS polymer and determine the acrylonitrile–butadiene–styrene ratio of the composite polymer. Confirmation of the presence of rubber domains is achieved by electron microscopy. Comparison with available physical property data serves to increase confidence in the identification or indicate the presence of unexpected structural features. Phase-seperation techniques can be used to provide detailed compositional analyses.

Processing. Good thermal stability plus shear thinning allow wide flexibility in viscosity control for a variety of processing methods. ABS exhibits non-Newtonian viscosity behavior. ABS can be processed by all the techniques used for other thermoplastics: compression and injection molding, extrusion, calendering, and blow-molding. Clean, under-graded regrind can be reprocessed in most applications (plating excepted), usually at 20% with virgin ABS. Post-processing operations include cold forming; thermoforming; metal plating; painting; hot stamping; ultrasonic, spin, and vibrational welding; and adhesive bonding.

TABLE 2. MATERIAL PROPERTIES OF GENERAL PURPOSE AND HEAT DISTORTION RESISTANT ABS

Properties	High impact	Medium impact	Heat resistant
notched Izod impact at RT, J/m[a]	347–534	134–320	107–347
tensile strength, MPa[b]	33–43	30–52	41–52
tensile modulus, GPa[c]	1.7–2.3	2.1–2.8	2.1–2.6
flexural modulus, GPa[c]	1.7–2.4	2.2–3.0	2.1–2.8
Rockwell hardness	80–105	105–112	100–111
heat deflection[d], °C at 455 kPa[e]	99–107	102–107	110–118
coefficient of linear thermal expansion, $\times 10^5$ cm/cm·°C	9.5–11.0	7.0–8.8	6.5–9.2
dielectric strength, kV/mm	16–31	16–31	14–34
dielectric constant, $\times 10^6$ Hz	2.4–3.8	2.4–3.8	2.4–3.8

[a] To convert J/m to ft · lb/in. divide by 53.4.
[b] To convert MPa to psi multiply by 145.
[c] To convert GPa to psi multiply by 145,000.
[d] Annealed.
[e] To convert kPa to psi multiply by 0.145.

TABLE 3. MARKETS FOR ABS PLASTICS BY REGION IN 1988, 10^3 T

	United states and canada	Western europe	Japan	Total	%
transportation	139	120	96	355	25
appliances	95	97	117	309	22
business machines	124	60	99	298	20
pipe and fittings	91	23		114	8
other	98	144	102	344	25
Total	*547*	*444*	*414*	*1405*	*100*

Applications

Its broad property balance and wide processing window have allowed ABS to become the largest selling engineering thermoplastic. ABS enjoys a unique position as a "bridge" polymer between commodity plastics and other higher performance engineering thermoplastics. Table 3 summarizes estimates for 1988 regional consumption of ABS resins by major use.

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ACRYLONITRILE-BUTADIENE RUBBER (ABR). See **Elastomers**.

ACTH. [CAS: 9002-60-2]. The adrenocorticotropic hormone of the anterior lobe of the pituitary gland, which specifically stimulates the adrenal cortex to secrete cortisone, and hence has effects identical with those of cortisone. ACTH differs in its chemistry, absorption, and metabolism from the other adrenal steroids. Chemically, it is a water-soluble polypeptide having a molecular weight of about 3500. Its complete amino acid sequence has been determined. It produces its peripheral physiological effects by causing discharge of the adrenocortical steroids into the circulation. ACTH has been extracted from pituitary glands. In purified form, ACTH is useful in treating some forms of arthritis, lupus erythematosus, and severe skin disorders. The action of ACTH injections parallels the result of large quantities of naturally formed cortisone if they were released naturally. See also **Steroids**.

ACTIN. One of the two proteins that makes up the myofibrils of striated muscles. The other protein is myosin. The combination of these two proteins is sometimes spoken of as actinomyosin. The banded nature of the myofibrils is due to the fact that both proteins are present where the bands are dark and only one or the other is present in the light bands. Since these bands lie side by side in the different myofibrils that go to make up a muscle fiber, the entire muscle fiber shows a banded or striated appearance. See also **Contractility and Contractile Proteins**.

ACTINIDE CONTRACTION. An effect analogous to the Lanthanide contraction, which has been found in certain elements of the Actinide series. Those elements from thorium (atomic number 90) to curium (atomic number 96) exhibit a decreasing molecular volume in certain compounds, such as those which the actinide tetrafluorides form with alkali metal fluorides, plotted in Fig. 1. The effect here is due to the decreasing crystal radius of the tetrapositive actinide ions as the atomic number increases. Note that in the Actinides the tetravalent ions are compared instead of the trivalent ones as in the case of the Lanthanides, in which the trivalent state is by far the most common.

The behavior is attributed to the entrance of added electrons into an (inner) *f* shell (4*f* for the Lanthanides, 5*f* for the Actinides) so that the increment they produce in atomic volume is less than the reduction due to the greater nuclear charge.

ACTINIDES AND TRANSACTINIDES

Actinides

The actinide elements are a group of chemically similar elements with atomic numbers 89 through 103, and their names, symbols, and atomic numbers are given in Table 1, see also **Radioactivity**; **Nuclear Power Technology**; **Plutonium**; **Thorium**; and **Uranium**. Each of the elements has a number of isotopes, all radioactive and some of which can be obtained in isotopically pure form.

Thorium, uranium, and plutonium are well known for their role as the basic fuels (or sources of fuel) for the release of nuclear energy. The importance of the remainder of the actinide group lies at present, for the most part, in the realm of pure research, but a number of practical applications are also known. The actinides present a storage-life problem in nuclear waste disposal and consideration is being given to separation methods for their recovery prior to disposal, see also **Nuclear Power Technology**.

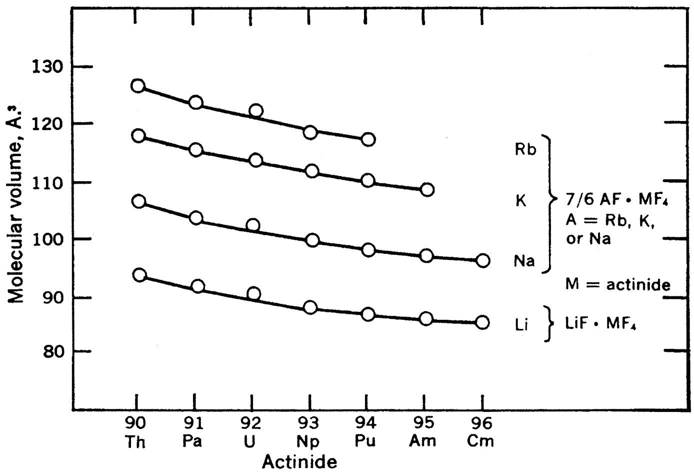

Fig. 1. Plot of molecular volume versus atomic number of the tetravalent Actinides

TABLE 1. THE ACTINIDE ELEMENTS

Atomic number	Element	Symbol	Atomic weight^a
89	actinium	Ac	227
90	thorium	Th	232
91	protactinium	Pa	231
92	uranium	U	238
93	neptunium	Np	237
94	plutonium	Pu	242
95	americium	Am	243
96	curium	Cm	248
97	berkelium	Bk	249
98	californium	Cf	249
99	einsteinium	Es	254
100	fermium	Fm	257
101	mendelevium	Md	258
102	nobelium	No	259
103	lawrencium	Lr	260

[a] Mass number of longest-lived or most available isotope.

Source

Only the members of the actinide group through Pu have been found to occur in nature. Thorium and uranium occur widely in the earth's crust in combination with other elements, and, in the case of uranium, in significant concentrations in the oceans. With the exceptions of uranium and thorium, the actinide elements are synthetic in origin for practical purposes, i.e., they are products of nuclear reactions. High neutron fluxes are available in modern nuclear reactors, and the most feasible method for preparing actinium, protactinium, and most of the actinide elements is through the neutron irradiation of elements of high atomic number.

Experimental Methods of Investigation. All of the actinide elements are radioactive and, except for thorium and uranium, special equipment and shielded facilities are usually necessary for their manipulation.

The study of the chemical behavior of concentrated preparations of short-lived isotopes is complicated by the rapid production of hydrogen peroxide in aqueous solutions and the destruction of crystal lattices in solid compounds. These effects are brought about by heavy recoils of high energy alpha particles released in the decay process.

Special techniques for experimentation with the actinide elements other than Th and U have been devised because of the potential health hazard to the experimenter and the small amounts available. In addition, investigations are frequently carried out with the substance present in very low concentration as a radioactive tracer. Tracer studies offer a method for obtaining knowledge of oxidation states, formation of complex ions, and the solubility of various compounds. These techniques are not applicable to crystallography, metallurgy, and spectroscopic studies. Microchemical or ultramicrochemical techniques are used extensively in chemical studies of actinide elements.

Electronic Structure. Measurements of paramagnetic susceptibility, paramagnetic resonance, light absorption, fluorescence, and crystal structure, in addition to a consideration of chemical and other properties, have provided a great deal of information about the electronic configuration of the aqueous actinide ions in which the electrons are in the $5f$ shell. There are exceptions, such as U_2S_3, and subnormal compounds, such as Th_2S_3, where $6d$ electrons are present.

Properties

The close chemical resemblance among many of the actinide elements permits their chemistry to be described for the most part in a correlative way.

Oxidation States. The oxidation states of the actinide elements are summarized in Table 2. The most stable states are designated by boldface type and those which are very unstable are indicated by parentheses.

The actinide elements exhibit uniformity in ionic types. Corresponding ionic types are similar in chemical behavior, although the oxidation–reduction relationships and therefore the relative stabilities differ from element to element.

Hydrolysis and Complex Ion Formation. Of the actinide ions, the small, highly charged M^{4+} ions exhibit the greatest degree of hydrolysis and complex ion formation.

The degree of hydrolysis or complex ion formation decreases in the order $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$. Presumably the relatively high tendency toward hydrolysis and complex ion formation of MO ions is related to the high concentration of charge on the metal atom. On the basis of increasing charge and decreasing ionic size, it could be expected that the degree of hydrolysis for each ionic type would increase with increasing atomic number.

Metallic State. The actinide metals, like the lanthanide metals, are highly electropositive. They can be prepared by the electrolysis of molten salts or by the reduction of a halide with an electropositive metal, such as calcium or barium. Their physical properties are summarized in Table 3.

Solid Compounds. Thousands of compounds of the actinide elements have been prepared, and the properties of some of the important binary compounds are summarized in Table 4.

Crystal Structure and Ionic Radii. Crystal structure data have provided the basis for the ionic radii (coordination number = CN = 6). For both M^{3+} and M^4 ions there is an actinide contraction, analogous to the lanthanide contraction, with increasing positive charge on the nucleus. As a consequence of the ionic character of most actinide compounds and of the similarity of the ionic radii for a given oxidation state, analogous compounds are generally isostructural.

Absorption and Fluorescence Spectra. The absorption spectra of actinide and lanthanide ions in aqueous solution and in crystalline form contain narrow bands in the visible, near-ultraviolet, and near-infrared regions of the spectrum.

TABLE 2. THE OXIDATION STATES OF THE ACTINIDE ELEMENTS

Atomic number and element														
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
						(2)			(2)	(2)	2	2	**2**	
3	(3)	(3)	3	3	3	**3**	**3**	**3**	**3**	**3**	**3**	**3**	3	**3**
	4	4	4	4	**4**	4	4	4	(4)					
		5	5	**5**	5	5								
			6	6	6	6								
				7	(7)									

TABLE 3. PROPERTIES OF ACTINIDE METALS

Element	Melting point, °C	Heat of vaporization, ΔH_v, kJ/mol (kcal/mol)	Boiling point, °C
actinium	1100 ± 50	293 (70)	
thorium	1750	564 (130)	3850
protactinium	1575		
uranium	1132	446.4 (106.7)	3818
neptunium	637 ± 2	418 (100)	3900
plutonium	646	333.5 (79.7)	3235
americium	1173	230 (55)	2011
curium	1345	386 (92.2)	3110
berkelium	1050		
californium	900 ± 30		
einsteinium	860 ± 30		

Transactinides

The elements beyond the actinides in the periodic table can be termed the transactinides. These begin with the element having the atomic number 104 and extend, in principle, indefinitely. Although only seven such elements, numbers 104–110 were definitely known in 2003, (Rutherfordium 104, Dubnium 105, Seaborgium 106, Bohrium 107, Hassium 108, Meitnerium 109, and Darmstadtium 110), there are good prospects for the discovery of a number of additional elements just beyond number 110 or in the region of larger atomic numbers. They are synthesized by the bomunderlinedment of heavy nuclides with heavy ions. See also **Chemical Elements**.

On the basis of the simplest projections it is expected that the half-lives of the elements beyond element 110 will become shorter as the atomic number is increased, and this is true even for the isotopes with the longest half-life for each element.

Turning to consideration of electronic structure, upon which chemical properties must be based, modern high speed computers have made possible the calculation of such structures. The calculations show that elements 104 through 112 are formed by filling the $6d$ electron subshell, which makes them, as expected, homologous in chemical properties with the elements hafnium ($Z = 72$) through mercury ($Z = 80$). Elements 113 through 118 result from the filling of the $7p$ subshell and are expected to be similar to the elements thallium ($Z = 81$) through radon ($Z = 86$).

It can be seen that elements in and near the island of stability based on element 114 can be predicted to have chemical properties as follows: element 114 should be a homologue of lead, that is, should be eka-lead; and element 112 should be eka-mercury, element 110 should be eka-platinum, etc. If there is an island of stability at element 126, this element and its neighbors should have chemical properties like those of the actinide and lanthanide elements.

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TABLE 4. PROPERTIES AND CRYSTAL STRUCTURE DATA FOR IMPORTANT ACTINIDE BINARY COMPOUNDS

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Density, g/mL
AcH_2	black		cubic	fluorite ($Fm3m$)	8.35
ThH_2	black		tetragonal	$F4/mmm$	9.50
Th_4H_{15}	black		cubic	$I4\bar{3}d$	8.25
α-PaH_3	gray		cubic	$Pm3n$	10.87
β-PaH_3	black		cubic	β-W	10.58
α-UH_3	?		cubic	$Pm3n$	11.12
β-UH_3	black		cubic	β-W ($Pm3n$)	10.92
NpH_2	black		cubic	fluorite	10.41
NpH_3	black		trigonal	$P\bar{3}c1$	9.64
PuH_2	black		cubic	fluorite	10.40
PuH_3	black		trigonal	$P\bar{3}c1$	9.61
AmH_2	black		cubic	fluorite	10.64
AmH_3	black		trigonal	$P\bar{3}c1$	9.76
CmH_2	black		cubic	fluorite	10.84
CmH_3	black		trigonal	$P\bar{3}c1$	10.06
BkH_2	black		cubic	fluorite	11.57
BkH_3	black		trigonal	$P\bar{3}c1$	10.44
Ac_2O_3	white		hexagonal	La_2O_3 ($P\bar{3}m1$)	9.19
Pu_2O_3	?		cubic	$Ia3$ (Mn_2O_3)	10.20
Pu_2O_3	black	2085	hexagonal	La_2O_3	11.47
Am_2O_3	tan		hexagonal	La_2O_3	11.77
Am_2O_3	reddish brown		cubic	$Ia3$	10.57
Cm_2O_3	white to faint tan	2260	hexagonal	La_2O_3	12.17
Cm_2O_3			monoclinic	$C2/m$ (Sm_2O_3)	11.90
Cm_2O_3	white		cubic	$Ia3$	10.80
Bk_2O_3	light green		hexagonal	La_2O_3	12.47
Bk_2O_3	yellow-green		monoclinic	$C2/m$	12.20
Bk_2O_3	yellowish brown		cubic	$Ia3$	11.66
Cf_2O_3	pale green		hexagonal	La_2O_3	12.69
Cf_2O_3	lime green		monoclinic	$C2/m$	12.37
Cf_2O_3	pale green		cubic	$Ia3$	11.39
Es_2O_3	white		hexagonal	La_2O_3	12.7
Es_2O_3	white		monoclinic $C2/m$	$C2/m$	12.4
Es_2O_3	white		cubic	$Ia3$	11.79
ThO_2	white	ca 3050	cubic	fluorite	10.00
PaO_2	black		cubic	fluorite	10.45
UO_2	brown to black	2875	cubic	fluorite	10.95
NpO_2	apple green		cubic	fluorite	11.14
PuO_2	yellow-green to brown	2400	cubic	fluorite	11.46
AmO_2	black		cubic	fluorite	11.68
CmO_2	black		cubic	fluorite	11.92
BkO_2	yellowish-brown		cubic	fluorite	12.31
CfO_2	black		cubic	fluorite	12.46
Pa_2O_5	white		cubic	fluorite-related	11.14
Np_2O_5	dark brown		monoclinic	$P2_1/c$	8.18
α-U_3O_8	black-green	1150 (dec)	orthorhombic	$C2mm$	8.39
β-U_3O_8	black-green		orthorhombic	$Cmcm$	8.32
γ-UO_3	orange	650 (dec)	orthorhombic	$Fddd$	7.80
$AmCl_2$	black		orthorhombic	$Pbnm$ ($PbCl_2$)	6.78
$CfCl_2$	red-amber		?		
$AmBr_2$	black		tetragonal	$SrBr_2$ ($P4/n$)	7.00
$CfBr_2$	amber		tetragonal	$SrBr_2$	7.22
ThI_2	gold		hexagonal	$P6_3/mmc$	7.45
AmI_2	black	ca 700	monoclinic	EuI_2 ($P2_1/c$)	6.60
CfI_2	violet		hexagonal	CdI_2 ($P\bar{3}m1$)	6.63
CfI_2	violet		rhombohedral	$CdCl_2$ ($R\bar{3}m$)	6.58
AcF_3	white		trigonal	LaF_3 ($P\bar{3}c1$)	7.88
UF_3	black	>1140(*dec*)	trigonal	LaF_3	8.95
NpF_3	purple		trigonal	LaF_3	9.12
PuF_3	purple	1425	trigonal	LaF_3	9.33
AmF_3	pink	1393	trigonal	LaF_3	9.53
CmF_3	white	1406	trigonal	LaF_3	9.85
BkF_3	yellow-green		orthorhombic	YF_3 ($Pnma$)	9.70
BkF_3	yellow-green		trigonal	LaF_3	10.15
CfF_3	light green		orthorhombic	YF_3	9.88
CfF_3	light green		trigonal	LaF_3	10.28
$AcCl_3$	white		hexagonal	UCl_3 ($P6_3/m$)	4.81
UCl_3	green	835	hexagonal	$P6_3/m$	5.50
$NpCl_3$	green	ca 800	hexagonal	UCl_3	5.60
$PuCl_3$	emerald green	760	hexagonal	UCl_3	5.71
$AmCl_3$	pink or yellow	715	hexagonal	UCl_3	5.87
$CmCl_3$	white	695	hexagonal	UCl_3	5.95
$BkCl_3$	green	603	hexagonal	UCl_3	6.02

(*continued overleaf*)

TABLE 4. (*continued*)

Compound	Color	Melting point, °C	Symmetry	Space group or structure type	Density, g/mL
α-$CfCl_3$	green	545	orthorhombic	$TbCl_3$ ($Cmcm$)	6.07
β-$CfCl_3$	green		hexagonal	UCl_3	6.12
$EsCl_3$	white to orange		hexagonal	UCl_3	6.20
$AcBr_3$	white		hexagonal	$UBr_3(P6_3/m)$	5.85
UBr_3	red	730	hexagonal	$P6_3/m$	6.55
$NpBr_3$	green		hexagonal	UBr_3	6.65
$NpBr_3$	green		orthorhombic	$TbCl_3(Cmcm)$	6.67
$PuBr_3$	green	681	orthorhombic	$TbCl_3$	6.72
$AmBr_3$	white to pale yellow		orthorhombic	$TbCl_3$	6.85
$CmBr_3$	pale yellow-green	625 ± 5	orthorhombic	$TbCl_3$	6.85
$BkBr_3$	light green		monoclinic	$AlCl_3(C2/m)$	5.604
$BkBr_3$	light green		orthorhombic	$TbCl_3$	6.95
$BkBr_3$	yellow green		rhombohedral	$FeCl_3$ ($R\bar{3}$)	5.54
$CfBr_3$	green		monoclinic	$AlCl_3$	5.673
$CfBr_3$	green		rhombohedral	$FeCl_3$	5.77
$EsBr_3$	straw		monoclinic	$AlCl_3$	5.62
PaI_3	black		orthorhombic	$TbCl_3$ ($Cmcm$)	6.69
UI_3	black		orthorhombic	$TbCl_3$	6.76
NpI_3	brown		orthorhombic	$TbCl_3$	6.82
PuI_3	green		orthorhombic	$TbCl_3$	6.92
AmI_3	pale yellow	ca 950	hexagonal	BiI_3 ($R\bar{3}$)	6.35
AmI_3	yellow		orthorhombic	$PuBr_3$	6.95
CmI_3	white		hexagonal	BiI_3	6.40
BkI_3	yellow		hexagonal	BiI_3	6.02
CfI_3	red-orange		hexagonal	BiI_3	6.05
EsI_3	amber to light yellow		hexagonal	BiI_3	6.18
ThF_4	white	1068	monoclinic	$UF_4(C2/c)$	6.20
PaF_4	reddish-brown		monoclinic	UF_4	6.38
UF_4	green	960	monoclinic	$C2/c$	6.73
NpF_4	green		monoclinic	UF_4	6.86
PuF_4	brown	1037	monoclinic	UF_4	7.05
AmF_4	tan		monoclinic	UF_4	7.23
CmF_4	light gray-green		monoclinic	UF_4	7.36
BkF_4	pale yellow-green		monoclinic	UF_4	7.55
CfF_4	light green		monoclinic	UF_4	7.57
α-$ThCl_4$	white		orthorhombic		4.12
β-$ThCl_4$	white	770	tetragonal	$UCl_4(I4_1/amd)$	4.60
$PaCl_4$	greenish-yellow		tetragonal	UCl_4	4.72
UCl_4	green	590	tetragonal	$I4_1/amd$	4.89
$NpCl_4$	red-brown	518	tetragonal	UCl_4	4.96
α-$ThBr_4$	white		tetragonal	$I4_1/a$	5.94
β-$ThBr_4$	white		tetragonal	UCl_4	5.77
$PaBr_4$	orange-red		tetragonal	UCl_4	5.90
UBr_4	brown	519	monoclinic	$2/c$-/-	
$NpBr_4$	dark red	464	monoclinic	$2/c$-/-	
ThI_4	yellow	556	monoclinic	$P2_1/n$	6.00
PaI_4	black				
UI_4	black				
PaF_5	white		tetragonal	$I\bar{4}2d$	
α-UF_5	grayish white		tetragonal	$I4/m$	5.81
β-UF_5	pale yellow		tetragonal	$I\bar{4}2d$	6.47
NpF_5			tetragonal	$I4/m$	
$PaCl_5$	yellow	306	monoclinic	$C2/c$	
α-UCl_5	brown		monoclinic	$P2_1/n$	3.81
β-UCl_5	red-brown		triclinic	$P\bar{1}$	
α-$PaBr_5$			monoclinic	$P2_1/c$	
β-$PaBr_5$	orange-brown		monoclinic	$P2_1/n$	
UBr_5	brown		monoclinic	$P2_1/n$	
PaI_5	black		orthorhombic		
UF_6	white	64.02[a]	orthorhombic	$Pnma$	5.060
NpF_6	orange	55	orthorhombic	$Pnma$	5.026
PuF_6	reddish-brown	52	orthorhombic	$Pnma$	4.86
UCl_6	dark green	178	hexagonal	$P\bar{3}m1$	3.62

[a] At 151.6 kPa; to convert kPa to atm, divide by 101.3.

ACTINIUM. [CAS: 7440-34-8]. Chemical element symbol Ac, at. no. 89, at. wt. 227 (mass number of the most stable isotope), periodic table group 3, classed in the periodic system as a higher homologue of lanthanum. The electronic configuration for actinium is

$$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^66d^17s^2$$

The ionic radius (Ac^{3+}) is 1.11Å.

Presently, 24 isotopes of actinium, with mass numbers ranging from 207 to 230, have been identified. All are radioactive. One year after the discovery of polonium and radium by the Curies, A. Debierne found an unidentified radioactive substance in the residue after treatment of pitchblende. Debierne named the new material *actinium* after the Greek word for ray. F. Giesel, independently in 1902, also found a radioactive material in the rare-earth extracts of pitchblende. He named this material *emanium*. In 1904, Debierne and Giesel compared the results of their experimentation and established the identical behavior of the two substances. Until formulation of the law of radioactive displacement by Fajans and Soddy about ten years later, however, actinium definitely could not be classed in the periodic system as a higher homologue of lanthanum.

The isotope discovered by Debierne and also noted by Giesel was ^{227}Ac which has a half-life of 21.7 years. The isotope results from the decay of ^{235}U (AcU-*actinouranium*) and is present in natural uranium to the extent of approximately 0.715%. The proportion of Ac/U in uranium ores is estimated to be approximately 2.10^{-10} at radioactive equilibrium. O. Hahn established the existence of a second isotope of actinium in nature, ^{228}Ac, in 1908. This isotope is a product of thorium decay and logically also is referred to as *meso*-thorium, with a half-life of 6.13 hours. The proportion of mesothorium to thorium ($MsTh_2$/Th) in thorium ores is about 5.10^{-14}. The other isotopes of actinium were found experimentally as the result of bombarding thorium targets. The half-life of 10 days of ^{225}Ac is the longest of the artificially produced isotopes. Although occurring in nature as a member of the neptunium family, ^{225}Ac is present in extremely small quantities and thus is very difficult to detect.

^{227}Ac can be extracted from uranium ores where present to the extent of 0.2 mg/ton of uranium and it is the only isotope that is obtainable on a macroscopic scale and that is reasonably stable. Because of the difficulties of separating ^{227}Ac from uranium ores, in which it accompanies the rare earths and with which it is very similar chemically, fractional crystallization or precipitation of relevant compounds no longer is practiced. Easier separations of actinium from lanthanum may be effected through the use of ion-exchange methods. A cationic resin and elution, mainly with a solution of ammonium citrate or ammonium-a-hydroxyisobutyrate, are used. To avoid the problems attendant with the treatment of ores, ^{227}Ac now is generally obtained on a gram-scale by the transmutation of radium by neutron irradiation in the core of a nuclear reactor. Formation of actinium occurs by the following process:

$$^{226}\mathrm{Ra}(n, \gamma)^{227}\mathrm{Ra} \xrightarrow{\beta-} {}^{227}\mathrm{Ac}$$

In connection with this method, the cross-section for the capture of thermal neutrons by radium is 23 barns (23×10^{-24} cm^2). Thus, prolonged radiation must be avoided because the accumulation of actinium is limited by the reaction ($\sigma = 500$ barns):

$$^{227}\mathrm{Ac}(n, \gamma)^{228}\mathrm{Ac}(\mathrm{MsTh_2}) \longrightarrow {}^{228}\mathrm{Th}(\mathrm{RdTh})$$

In 1947, F. Hageman produced 1 mg actinium by this process and, for the first time, isolated a pure compound of the element. It has been found that when 25 g of $RaCO_3$ (radium carbonate) are irradiated at a flux of 2.6×10^{14} ncm^{-2} s^{-1} for a period of 13 days, approximately 108 mg of ^{227}Ac (8 Ci) and 13 mg of ^{228}Th (11 Ci) will be yielded. In an intensive research program by the Centre d'Etude de l'Energie Nucléaire Belge, Union Minière, carried out in 1970–1971, more than 10 g of actinium were produced. The process is difficult for at least two reasons: (1) the irradiated products are highly radioactive, and (2) radon gas, resulting from the disintegration of radium, is evolved. The methods followed in Belgium for the separation of ^{226}Ra, ^{227}Ac, and ^{228}Th involved the precipitation of $Ra(NO_3)_2$ (radium nitrate) from concentrated HNO_3 after which followed the elimination of thorium by adsorption on a mineral ion exchanger (zirconium phosphate) which withstand high levels of radiation without decomposition.

Metallic actinium cannot be obtained by electrolytic means because it is too electropositive. It has been prepared on a milligram-scale through the reduction of actinium fluoride in a vacuum with lithium vapor at about 350°C. The metal is silvery white, faintly emits a blue-tinted light which is visible in darkness because of its radioactivity. The metal takes the form of a face-centered cubic lattice and has a melting point of 1050 ± 50°C. By extrapolation, it is estimated that the metal boils at about 3300°C. An amalgam of metallic actinium may be prepared by electrolysis on a mercury cathode, or by the action of a lithium amalgam on an actinium citrate solution (pH = 1.7 to 6.8).

In chemical behavior, actinium acts even more basic than lanthanum (the most basic element of the lanthanide series). The mineral salts of actinium are extracted with difficulty from their aqueous solutions by means of an organic solvent. Thus, they generally are extracted as chelates with trifluoroacetone or diethylhexylphosphoric acid. The water-insoluble salts of actinium follow those of lanthanum, namely, the carbonate, fluoride, fluosilicate, oxalate, phosphate, double sulfate of potassium. With exception of the black sulfide, all actinium compounds are white and form colorless solutions. The crystalline compounds are isomorphic.

In addition to its close resemblance to lanthanum, actinium also is analogous to curium ($Z = 96$) and lawrencium ($Z = 103$), both of the group of trivalent transuranium elements. This analogy led G.T. Seaborg to postulate the actinide theory, wherein actinium begins a new series of rare earths which are characterized by the filling of the 5f inner electron shell, just as the filling of the 4f electron shell characterizes the Lanthanide series of elements. However, the first elements of the Actinide series differ markedly from those of actinium. Notably, there is a multiplicity of valences for which there is no equivalent among the lanthanides. See **Chemical Elements** for other properties of actinium.

Mainly, actinium has been of interest from a scientific standpoint. However, ^{227}Ac has been proposed as a source of heat in space vehicles. It is interesting to note that the heat produced from the absorption of the radiation emitted by 1 g of actinium, when in equilibrium with its daughters, is 12,500 cal/hour.

See also **Actinide Contraction**.

Additional Reading

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ACTINOLITE. The term for a calcium-iron-magnesium amphibole, the formula being $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ but the amount of iron varies considerably. It occurs as bladed crystals or in fibrous or granular masses. Its hardness is 5–6, sp gr 3–3.2, color green to grayish green, transparent to opaque, luster vitreous to silky or waxy. Iron in the ferrous state is believed to be the cause of its green color. Actinolite derives its name from the frequent radiated groups of crystals. Essentially it is an iron-rich tremolite; the division between the two minerals is quite arbitrary, with color the macroscopic definitive factor—white for tremolite, green for actinolite. Actinolite is found in schists, often with serpentine, and in igneous rocks, probably as the result of the alteration of pyroxene. The schists of the Swiss Alps carry actinolite. It is also found in Austria, Saxony, Norway, Japan, and Canada in the provinces of Quebec and Ontario. In the United States actinolite occurs in Massachusetts, Pennsylvania, Maryland, and as a zinc-manganese bearing variety in New Jersey. See also **Amphibole**; **Tremolite**; and **Uralite**.

ACTINON. The name of the isotope of radon (emanation), which occurs in the naturally occurring actinium, series being, produced by alpha-decay of actinium X, which is itself a radium isotope. Actinon has an atomic number of 86, a mass number of 219, and a half-life of 3.92 seconds, emitting an alpha particle to form polonium-215 (Actinium A). See also **Chemical Elements**; and **Radioactivity**.

ACTIVATED SLUDGE. This is the biologically active sediment produced by the repeated aeration and settling of sewage and/or organic wastes. The dissolved organic matter acts as food for the growth of an aerobic flora. This flora produces a biologically active sludge which is usually brown in color and which destroys the polluting organic matter in the sewage and waste. The process is known as the activated sludge process.

The activated sludge process, with minor variations, consists of aeration through submerged porous diffusers or by mechanical surface agitation, of either raw or settled sewage for a period of 2–6 hours, followed by settling of the solids for a period of 1–2 hours. These solids, which are made up of the solids in the sewage and the biological growths which develop, are returned to the sewage flowing into the aeration tanks. As this cycle is repeated, the aerobic organisms in the sludge develop until there is 1000–3000 ppm of suspended sludge in the aeration liquor. After a while more of the active sludge is developed than is needed to purify the incoming sewage, and this excess is withdrawn from the process and either dried for fertilizer or digested anaerobically with raw sewage sludge. This anaerobic digestion produces a gas consisting of approximately 65% methane and 35% CO_2, and changes the water-binding properties so that the sludge is easier to filter or dry.

The activated sludge is made up of a mixture of zoogleal bacteria, filamentous bacteria, protozoa, rotifera, and miscellaneous higher forms of life. The types and numbers of the various organisms will vary with the types of food present and with the length of the aeration period. The settled sludge withdrawn from the process contains from 0.6 to 1.5% dry solids, although by further settling it may be concentrated to 3–6% solids. Analysis of the dried sludge for the usual fertilizer constituents show that it contains 5–6% of slowly available N and 2–3% of P. The fertilizing value appears to be greater than the analysis would indicate, thus suggesting that it contains beneficial trace elements and growth-promoting compounds. Recent developments indicate that the sludge is a source of vitamin B_{12}, and has been added to mixed foods for cattle and poultry.

The quality of excess activated sludge produced will vary with the food and the extent of oxidation to which the process is carried. In general, about 1 part sludge is produced for each part organic matter destroyed. Prolonged or over-aeration will cause the sludge to partially disperse and digest itself. The amount of air or more precisely oxygen that is necessary to keep the sludge in an active and aerobic condition depends on the oxygen demand of the sludge organisms, the quantity of active sludge, and the amount of food to be utilized. Given sufficient food and sufficient organisms to eat the food, the process seems to be limited only by the rate at which oxygen or air can be dissolved into the mixed liquor. This rate depends on the oxygen deficit, turbulence, bubble size, and temperature and at present is restricted by the physical methods of forcing the air through the diffuser tubers and/or mechanical agitation.

In practice, the excess activated sludge is conditioned with 3–6% $FeCl_3$ and filtered on vacuum filters. This reduces the moisture to about 80% and produces a filter cake which is dried in rotary or spray driers to a moisture content of less than 5%. It is bagged and sold direct as a fertilizer, or to fertilizer manufacturers who use it in mixed fertilizer.

The mechanism of purification of sewage by the activated sludge is two-fold i.e., (1) absorption of colloidal and soluble organic matter on the floc with subsequent oxidation by the organisms, and (2) chemical splitting and oxidation of the soluble carbohydrates and proteins to CO_2, H_2O, NH_3, NO_2, NO_3, SO_4, PO_4 and humus. The process of digestion proceeds by hydrolysis, decarboxylation, deaminization and splitting of S and P from the organic molecules before oxidation.

The process is applicable to the treatment of almost any type of organic waste waters which can serve as food for biological growth. It has been applied to cannery wastes, milk products wastes, corn products wastes, and even phenolic wastes. In the treatment of phenolic wastes a special flora is developed which thrives on phenol as food.

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ACTIVATION (Molecular). When a molecule which is a Lewis base forms a coordinate bond with a metal ion or with a molecular Lewis acid (such as $AlCl_3$ or BF_3), its electronic density pattern is altered, and with this, the ease with which it undergoes certain reactions. In some instances the polarization that ensues is sufficient to lead to the formation of ions by a process of the type

$$A{:}B{:} + M = A^+ + {:}B{:}M^-$$

More commonly the molecule is polarized by coordination in such a manner that A bears a partial positive charge and B a partial negative charge in a complex A:B:M. Where M is a reducible or oxidizable metal ion, an electron-transfer process may result in which a free radical is generated from A:B: or its fragments and the metal assumes a different oxidation state. In any case the resulting species is often in a state in which it undergoes one or more types of chemical reaction much more readily.

Theoretical Basis

The theoretical basis underlying these activation processes is in the description of the bonding which occurs between the ligand (Lewis base) and the coordination center. This consists of variable contributions from two types of bond. The first is from the sigma bond in which both the electrons in the bonding orbital come from the ligand. This kind of bonding occurs with ligands with available lone pairs (as NH_3, H_2O and their derivatives) and leads to a depletion of electronic charge from the substrate. The second is from the pi bond; here the electrons may come from the metal (if it is a transition metal with suitably occupied d orbitals) or from the ligand (where it has filled *p* orbitals or molecular orbitals of suitable symmetry). In this case the electronic shifts may partially compensate those arising from the sigma bond if the metal "back-donates" electrons to the ligand. Such shifts may also accentuate those of sigma bonding where ligand electrons are used for both bonds. It is generally found that the net drift of the electronic density is *away* from the ligand.

Activation of Electrophiles

The activation of electrophiles by coordination is a direct result of the weakening of the bond between the donor atom and the rest of the ligand molecule after the donor atom has become bonded to the coordination center. There is considerable evidence to support the claim that this bond need not be broken heterolytically prior to reaction as an electrophile. When this does not occur the literal electrophile is that portion of the ligand which bears a partial positive charge. In such a case the activation process can be more accurately represented by:

$$A{:}B{:} + M = \overset{\delta+}{A}{:}\overset{\delta-}{B}{:}M$$

Examples of this type of process are:

A:B:	+	M	→	$\overset{\delta+}{A}{:}\overset{\delta-}{B}{:}M$
Cl:Cl:		$FeCl_3$		$Cl{:}Cl{:}FeCl_3$
NC:Cl:		$AlCl_3$		$NC{:}Cl{:}AlCl_3$
$\underset{\underset{O}{\|}}{RC}{:}Cl{:}$		$AlCl_3$		$\underset{\underset{O}{\|}}{RC}{:}Cl{:}AlCl_3$
$O_2N{:}Cl{:}$		$AlCl_3$		$O_2N{:}Cl{:}AlCl_3$
$\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{RS}}{:}Cl{:}$		$AlCl_3$		$\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{RS}}{:}Cl{:}AlCl_3$
R:Cl:		BF_3		$R{:}Cl{:}BF_3$

The resultant electrophiles are effective attacking species and can be used to replace an aromatic hydrogen by the group A. When coordination is used to activate an electrophile which has additional donor groups not involved in the principal reaction, and if these are sufficiently effective as donors, they will react with the coordination centers initially added and stop the activation process. In these cases a larger amount of the Lewis acid must be added so that there is more than enough to complex with all the uninvolved donor groups. The extra reagent then provides the Lewis acid needed for the activation process. This is encountered in the Fries reaction and in Friedel-Crafts reactions where the substrate has additional coordination sites. This particular procedure is also used in the "swamping catalyst" procedure for the catalytic halogenation of aromatic compounds.

The usual activation of carbon monoxide by coordination appears to involve complexes in which the carbon atom bonded to the metal is rendered slightly positive, and thus more readily attacked by electron rich species such as ethylenic or acetylenic linkages. An example is seen in the reaction of nickel carbonyl and aqueous acetylene, which results in the production of acrylic acid.

Activation of Free Radicals

The formation of free radicals results from a very similar process when the species M can be oxidized or reduced in a one-electron step with the resultant heterolytic splitting of the A:B bond. The basic reaction in an oxidation reaction of this sort is

$$\mathrm{A{:}B{:}} + \mathrm{M}^{+x} = \mathrm{A}\cdot + \mathrm{{:}B{:}M}^{+x+1}$$

where A and B may be the same or different. The most thoroughly characterized of these reactions is the one found with Fenton's reagent:

$$\mathrm{Fe}^{2+} + \mathrm{HOOH} = \mathrm{HO}\cdot + \mathrm{Fe\ (OH)}^{2+}.$$

The resultant hydroxyl radicals are effective in initiating many chain reactions. The number of metal ions and complexes which are capable of activating hydrogen peroxide in this manner is quite large and is determined in part by the redox potentials of the activator. Related systems in which free radicals are generated by the intervention of suitable metallic catalysts include many in which oxygen is consumed in autoxidations. Cobalt(II) compounds which act as oxygen carriers can often activate radicals in such systems by reactions of the type:

$$\mathrm{Co(II)L} + \mathrm{O}_2 = \mathrm{Co(III)L} + \mathrm{O}_2^-, \text{ etc.}$$

Processes of this sort have been used for catalytic oxidations and in cases where a complex with O_2 is formed, the reversibility of the reaction has been studied as a potential process for separating oxygen from the atmosphere.

Radical generating systems of this sort may be used for the initiation of many addition polymerization reactions including those of acrylonitrile and unsaturated hydrocarbons. The information on systems other than those derived from hydrogen peroxide is very meager.

The activation of O_2 by low oxidation states of plantinum has also been demonstrated in reactions such as

$$2\mathrm{P(C_6H_5)_3} + \mathrm{O_2} \xrightarrow{\mathrm{Pt(P(C_6H_5)_3)_3}} 2\mathrm{(C_6H_5)_3PO}.$$

Ligands such as ethylene are Lewis basesby virtue of the availability of the electrons of their pi bonds to external reagents and the coordination of unsaturated organic compounds to species such as Cu(I), Ag(I), Pd(II), and Pt(II) is a well established phenomenon. The coordination process with such ligands usually involves a considerable element of back bonding from the filled d orbitals of the metal ion. The coordination process activates olefins towards cis-trans isomerizations and attach by reagents such as hydrogen halides. Coordination to palladium(II) facilitates attach of olefins by water via a redox process as seen in the Smid reaction:

$$\mathrm{PdCl_2} + \mathrm{H_2C{=}CH_2} + \mathrm{H_2O} = \mathrm{Pd} + \mathrm{CH_3CHO} + 2\mathrm{HCl}$$

$$\mathrm{Pd} + 2\mathrm{CuCl_2} = 2\mathrm{CuCl} + \mathrm{PdCl_2}$$

$$2\mathrm{HCl} + 2\mathrm{CuCl} + \tfrac{1}{2}\mathrm{O_2} = 2\mathrm{CuCl_2} + \mathrm{H_2O}$$

A similar reaction also occurs for carbon monoxide:

$$\mathrm{Pd}^{2+} + \mathrm{CO} + \mathrm{H_2O} = \mathrm{Pd} + \mathrm{CO_2} + 2\mathrm{H}^+.$$

Activation of nucleophiles by coordination, best exemplified by various complexes used as catalysts for hydrogenation, and coordination assistance to photochemical activation, may be similarly demonstrated.

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ACTIVATOR. 1. A substance that renders a material or a system reactive; commonly, a catalyst. 2. A special use of this term occurs in the flotation process, where an activator assists the action of the collector. 3. An impurity atom, present in a solid, that makes possible the effects of luminescence, or markedly increases their efficiency. Examples are copper in zinc sulfide, and thallium in potassium chloride. See also **Enzyme**.

ACTIVE CENTER. Atoms which, by their position on a surface, such as at the apex of a peak, at a step on the surface or a kink in a step, or on the edge or corner of a crystal, share with neighboring atoms an abnormally small portion of their electrostatic field, and therefore have a large residual field available for catalytic activity or for adsorption.

ACTIVE DEPOSIT. The name given to the radioactive material that is deposited on the surface of any substance placed in the neighborhood of a preparation containing any of the naturally occurring radioactive chains (uranium, thorium, or actinium chains). This deposit results from deposition of the nongaseous products of the gaseous radon nuclides that have escaped from the parent substance. An active deposit can be concentrated on a negatively charged metal wire or surface placed in closed vessels containing the radon. See also **Radioactivity**.

ACTIVITY COEFFICIENT. A fractional number which when multiplied by the molar concentration of a substance in solution yields the chemical activity. This term provides an approximation of how much interaction exists between molecules at higher concentrations. Activity coefficients and activities are most commonly obtained from measurements of vapor-pressure lowering, freezing-point depression, boiling-point elevation, solubility, and electromotive force. In certain cases, activity coefficients can be estimated theoretically. As commonly used, activity is a relative quantity having unit value in some chosen standard state. Thus, the standard state of unit activity for water, a_w, in aqueous solutions of potassium chloride is pure liquid water at one atmosphere pressure and the given temperature. The standard state for the activity of a solute like potassium chloride is often so defined as to make the ratio of the activity to the concentration of solute approach unity as the concentration decreases to zero.

In general, the activity coefficient of a substance may be defined as the ratio of the effective contribution of the substance to a phenomenon to the actual contribution of the substance to the phenomenon. In the case of gases the effective pressure of a gas is represented by the fugacity f and the actual pressure of the gas by P. The activity coefficient, γ, of the gas is given by

$$\gamma = f/P. \tag{1}$$

One method of calculating fugacity and hence γ is based on the measured deviation of the volume of a real gas from that of an ideal gas. Consider the case of a pure gas. The free energy F and chemical potential μ changes with pressure according to the equation

$$dF = d\mu = V\,dP. \tag{2}$$

but by definition

$$d\mu = V\,dP = RT\ d\ln f \tag{3}$$

If the gas is ideal, the molal volume V_i is given by

$$V_i = \frac{RT}{P} \tag{4}$$

but for a nonideal gas this is not true. Let the molal volume of the nonideal gas be V_n and define the quantity α by the equation

$$\alpha = V_i - V_n = \frac{RT}{P} - V_n \tag{5}$$

Then V of Eq. (2) is V_n of Eq. (5) and hence from Eq. (5)

$$V = \frac{RT}{P} - \alpha \tag{6}$$

Therefore from Eqs. (2), (3), and (6)

$$RT\ d\ln f = dF = d\mu = RT\ D\ln P - \alpha\,dP \tag{7}$$

and

$$RT\ln f = RT\ln P - \int_0^P \alpha\,dP \tag{8}$$

Thus knowing PVT data for a gas it is possible to calculate f. The integral in Eq. (8) can be evaluated graphically by plotting α, the deviation of gas volume from ideality, versus P and finding the area under the curve out to the desired pressure. Also it may be found by mathematically relating α to P by an equation of state, or by using the method of least squares or other acceptable procedure the integral may be evaluated analytically for any value of P. The value of f at the desired value of P may thus be found and consequently the activity coefficient calculated. Other methods are available for the calculation of f and hence of γ, the simplest perhaps being the relationship

$$f = \frac{P^2}{P_i} \tag{9}$$

where P_i is the ideal and P the actual pressure of the gas.

In the case of nonideal solutions, we can relate the activity α_A of any component A of the solution to the chemical potential μ_A of that component by the equation

$$\mu_A = \mu_A^{\circ\prime} + RT \ln a_A \tag{10}$$

$$= \mu_A^{\circ\prime} + RT \ln \gamma_A X_A \tag{11}$$

where $\mu_A^{\circ\prime}$ is the chemical potential in the reference state where a_i is unity and is a function of temperature and pressure only, whereas γ_A is a function of temperature pressure and concentration. It is necessary to find the conditions under which γ_A is unity in order to complete its definition. This can be done using two approaches—one using Raoult's law which for solutions composed of two liquid components is approached as $X_A \to 1$; and two using Henry's law which applies to solutions, one component of which may be a gas or a solid and which is approached at $X_A \to 0$. Here X_A represents the mole fraction of component A.

For liquid components using Raoult's law

$$\gamma_A \to 1 \text{ as } X_A \to 1 \tag{12}$$

Since the logarithmic term is zero in Eq. (11) under this limiting condition, $\mu_A^{\circ\prime}$ is the chemical potential of pure component A at the temperature and pressure under consideration. For ideal solutions the activity coefficients of both components will be unity over the whole range of composition.

The convention using Henry's law is convenient to apply when it is impossible to vary the mole fraction of both components up to unity. Solvent and solute require different conventions for such solutions. As before, the activity of the solvent, usually taken as the component present in the higher concentration, is given by

$$\gamma_A \to 1 \text{ as } X_A \to 0 \tag{14}$$

Thus, $\mu_A^{\circ\prime}$ for the solute in Eq. (11) is the chemical potential of the solute in a hypothetical standard state in which the solute at unit concentration has the properties which it has at infinite dilution.

γ_A is the activity coefficient of component A in the solution and is given by the expression

$$\gamma_A = \frac{a_A}{X_A} \tag{15}$$

In Eq. (15) a_A is the activity or in a sense the effective mole fraction of component A in the solution.

The activity a_A of a component A in solution may be found by considering component A as the solvent. Then its activity at any mole fraction is the ratio of the partial pressure of the vapor of A in the solution to the vapor pressure of pure A. If B is the solute, its standard reference state is taken as a hypothetical B with properties which it possesses at infinite dilution.

The equilibrium constant for the process

$$B \text{ (gas)} \leftrightarrow B \text{ (solution)} \tag{16}$$

is

$$K = \frac{a_{\text{solution}}}{a_{\text{gas}}} \tag{17}$$

Since the gas is sufficiently ideal its activity a_{gas} is equivalent to its pressure P_2. Since the solution is far from ideal, the activity a_{solute} of the liquid B is not equal to its mole fraction N_2 in the solution. However,

$$K' = N_2/P_2 \tag{18}$$

and extrapolating a plot of this value versus N_2 to $N_2 = 0$ one obtains the ratio where the solution is ideal. This extrapolated value of K' is the true equilibrium constant K when the activity is equal to the mole fraction

$$K = a_2/P_2 \tag{19}$$

Thus a_2 can be found. The methods involved in Eqs. (16) through (19) arrive at the activities directly and thus obviate the determination of the activity coefficient. However, from the determined activities and known mole fractions γ can be found as indicated in Eq. (15).

In the case of ions the activities, a_+ and a_- of the positive and negative ions, respectively, are related to the activity, a, of the solute as a whole by the equation

$$a_+^p \times a_-^q \tag{20}$$

and the activity coefficients γ_+ and γ_- of the two charge types of ions are related to the molality, m, of the electrolyte and ion activities a_+ and a_- by the equations

$$\gamma_+ = \frac{a_+}{pm}; \quad \gamma_- = \frac{a_-}{qm} \tag{21}$$

Also the activity coefficient of the electrolyte is given by the equation

$$\gamma = (\gamma_+^p \times \gamma_-^q)^{(1/p+q)} \tag{22}$$

In Eqs. (20), (21) and (22) p and q are numbers of positive and negative ions, respectively, in the molecule of electrolyte. In dilute solutions it is considered that ionic activities are equal for uni-univalent electrolytes, i.e., $\gamma_+ = \gamma_-$.

Consider the case of $BaCl_2$.

$$\gamma = (\gamma_+ \times \gamma^2)^{(1/1+2)} = (\gamma_+ \times \gamma_-^2)^{1/3} \tag{23}$$

or

$$\gamma^3 = \gamma_+ \gamma_-^2 \tag{24}$$

also

$$a = a_+ \times a_-^2 = (m\gamma_+)(2m\gamma_-)^2 \tag{25}$$

$$= 4\, m^3 \gamma_+ \gamma_-^2 = 4\, m^3 \gamma^3 \tag{26}$$

Activity coefficients of ions are determined using electromotive force, freezing point, and solubility measurements or are calculated using the theoretical equation of Debye and Hückel.

The solubility, s, of AgCl can be determined at a given temperature and the activity coefficient γ determined at that temperature from the solubility and the solubility product constant K. Thus

$$K = a_+ a_- = \gamma_+ c_+ \gamma_- c_- \tag{27}$$

where c_+ and c_- are the molar concentrations of the positive silver and negative chloride ions, respectively. The solubility s of the silver chloride is simply $s = c_+ = c_-$. The expression for K is then

$$K = \gamma^2 s^2 \tag{28}$$

and

$$\gamma = \frac{K^{1/2}}{s} \tag{29}$$

By measuring the solubility, s, of the silver chloride in different concentration of added salt and extrapolating the solubilities to zero salt concentration, or better, to zero ionic strength, one obtains the solubility when $\gamma = 1$, and from Eq. (29) K can be found. Then γ can be calculated using this value of K and any measured solubility. Actually, this method is only applicable to sparingly soluble salts. Activity coefficients of ions and of electrolytes can be calculated from the Debye-Hückel equations. For a uni-univalent electrolyte, in water at 25°C, the equation for the activity coefficient of an electrolyte is

$$\log \gamma = -0.509 z_+ z_- \sqrt{\mu} \tag{30}$$

where z_+ and z_- are the valences of the ion and μ is the ionic strength of the solution, i.e.,

$$\mu = \tfrac{1}{2} \Sigma c_i z_i^2 \tag{31}$$

where c_i is the concentration and z_i the valence of the ith type of ion.

To illustrate a use of activity coefficients, consider the cell without liquid junction

$$\text{Pt, } H_2\text{(g); HCl (m); AgCl, Ag} \tag{32}$$

for which the chemical reaction is

$$\tfrac{1}{2} H_2\text{(g)} + \text{AgCl (solid)} = \text{HCl (molality, m)} + \text{Ag (solid.)} \tag{33}$$

The electromotive force, E, of this cell is given by the equation

$$E = E^\circ - \frac{2.303\, RT}{n\mathbf{F}} \log \frac{a_{\text{HCl}}}{P_{H_2}}$$

$$= E^\circ - 0.05915 \log m^2 \gamma^2 \tag{34}$$

where E° is the standard potential of the cell, n is the number of electrons per ion involved in the electrode reaction (here $n = 1$), $\mathbf{F}$ is the coulombs per faraday, a (equal to $m^2\gamma^2$) is the activity of the electrolyte HCl, P_{H_2} is the pressure (1 atm) and is equal to the activity of the hydrogen gas, and AgCl (solid) and Ag (solid) have unit activities. Transferring the exponents in front of the logarithmic term in Eq. (34), the equation can be written,

$$E = E^\circ - 0.1183 \log m - 0.1183 \log \gamma \tag{35}$$

which by transposing the log m term to the left of the equation becomes

$$E + 0.1183 \log m = E^\circ - 0.1183 \log \gamma \tag{36}$$

For extrapolation purposes, the extended form of the Debye-Hückel equation involving the molality of a dilute univalent electrolyte in water at 25°C is used:

$$\log \gamma = -0.509\sqrt{m} + bm \tag{37}$$

where b is an empirical constant.

Substitution of $\log \gamma$ from Eq. (37) into Eq. (36) gives

$$\begin{aligned} E + 0.1183 \log m - 0.0602\ m^{1/2} \\ = E^\circ - 0.1183\ bm \end{aligned} \tag{38}$$

A plot of the left hand side of Eq. (38) versus m yields a practically straight line, the extrapolation of which to $m = 0$ gives E° the standard potential of the cell. This value of E° together with measured values of E at specified m values can be used to calculate γ for HCl in dilute aqueous solutions at 25° for different m − values. Similar treatment can be applied to other solvents and other solutes at selected temperatures.

Activity coefficients are used in calculation of equilibrium constants, rates of reactions, electrochemical phenomena, and almost all quantities involving solutes or solvents in solution.

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ACTIVITY (Radioactivity). The activity of a quantity of radioactive nuclide is defined by the ICRU as $\Delta N/\Delta t$, where N is the number of nuclear transformations that occur in this quantity in time Δt. The symbol Δ preceding the letters N and t denotes that these letters represent quantities that can be deduced only from multiple measurements that involve averaging procedures. The special unit of activity is the curie, defined as exactly 3.7×10^{10} transformations per second. See **Radioactivity**.

ACTIVITY SERIES. Also referred to as the *electromotive series* or the *displacement series*, this is an arrangement of the metals (other elements can be included) in the order of their tendency to react with water and acids, so that each metal displaces from solution those below it in the series and is displaced by those above it. See Table 1. Since the electrode potential of a metal in equilibrium with a solution of its ions cannot be measured directly, the values in the activity series are, in each case, the difference between the electrode potential of the given metal (or element) in equilibrium with a solution of its ions, and that of hydrogen in equilibrium with a solution of its ions. Thus in the table, it will be noted that hydrogen has a value of 0.000. In experimental procedure, the hydrogen electrode is used as the standard with which the electrode potentials of other substances are compared. The theory of displacement plays a major role in electrochemistry and corrosion engineering. See also **Corrosion**; and **Electrochemistry**.

ACYL. An organic radical of the general formula, RCO−. These radicals are also called acid radicals, because they are often produced from organic acids by loss of a hydroxyl group. Typical acyl radicals are acetyl, CH_3CO-, benzyl, C_6H_5CO-, etc.

ACYLATION. A reaction or process whereby an acyl radical, such as acetyl, benzoyl, etc., is introduced into an organic compound. Reagents often used for acylation are the acid anhydride, acid chloride, or the acid of the particular acyl radical to be introduced into the compound.

TABLE 1. STANDARD ELECTRODE POTENTIALS (25°C)

Reaction		Volts
$Li^+ + e^-$	$\rightleftharpoons Li$	−3.045
$K^+, +e^-$	$\rightleftharpoons K$	−2.924
$Ba^{2+} + 2e^-$	$\rightleftharpoons Ba$	−2.90
$Ca^{2+} + 2e^-$	$\rightleftharpoons Ca$	−2.76
$Na^+ + e^-$	$\rightleftharpoons Na$	−2.711
$Mg^{2+} + 2e^-$	$\rightleftharpoons Mg$	−2.375
$Al^{3+} + 3e^-$	$\rightleftharpoons Al$	−1.706
$2H_2O + 2e^-$	$\rightleftharpoons H_2 + 2\ OH^-$	−0.828
$Zn^{2+} + 2e^-$	$\rightleftharpoons Zn$	−0.763
$Cr^{3+} + 3e^-$	$\rightleftharpoons Cr$	−0.744
$Fe^{2+} + 2e^-$	$\rightleftharpoons Fe$	−0.41
$Cd^{2+} + 2e^-$	$\rightleftharpoons Cd$	−0.403
$Ni^{2+} + 2e^-$	$\rightleftharpoons Ni$	−0.23
$Sn^{2+} + 2e^-$	$\rightleftharpoons Sn$	−0.136
$Pb^{2+} + 2e^-$	$\rightleftharpoons Pb$	−0.127
$2H^+ + 2e^-$	$\rightleftharpoons H_2$	0.000
$Cu^{2+} + 2e^-$	$\rightleftharpoons Cu$	+0.34
$I_2 + 2e^-$	$\rightleftharpoons 2I^-$	+0.535
$Fe^{3+} + e^-$	$\rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + e^-$	$\rightleftharpoons Ag$	+0.799
$Hg^{2+} + 2e^-$	$\rightleftharpoons Hg$	+0.851
$Br_2 + 2e^-$	$\rightleftharpoons 2Br$	+1.065
$O_2 + 4H^+ + 4e^-$	$\rightleftharpoons 2H_2O$	+1.229
$Cr_2O_7{}^{2-}\ +14H^+ + 6e^-$	$\rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2(gas) + 2e^-$	$\rightleftharpoons 2Cl$	+1.358
$Au^{3+} + 3e^-$	$\rightleftharpoons Au$	+1.42
$MnO_4{}^- + 8H^+ + 5e^-$	$\rightleftharpoons Mn^{2+} + 4H_2O$	+1.491
$F_2 + 2e^-$	$\rightleftharpoons 2F^-$	+2.85

ADAMANTINE COMPOUND. A compound having in its crystal structure an arrangement of atoms essentially that of diamond, in which every atom is linked to its four neighbors mainly by covalent bonds. An example is zinc sulfide, but it is to be noted that the eight electrons involved in forming the four bonds are not provided equally by the zinc and sulfur atoms, the sulfur yielding its six valence electrons, and the zinc, two. This is the structure of typical semiconductors, e.g., silicon and germanium.

ADAMS, ROGER (1889–1971). An American chemist, born in Boston; graduated from Harvard, where he taught chemistry for some years. After studying in Germany, he move to the University of Illinois in 1916, where he later became chairman of the department of chemistry (1926–1954). During his prolific career, he made this department one of the best in the country, and strongly influenced the development of industrial chemical research in the U.S. His executive and creative ability made him an outstanding figure as a teacher, innovator, and administrator. Among his research contributions were development of platinum-hydrogenation catalysts, and structural determinations of chaulmoogric acid, gossypol, alkaloids, and marijuana. He held many important offices, including president of the ACS and AAS, and was a recipient of the Priestley medal.

ADDITIVE COLOR PROCESS. An early system of color imagery in which the color synthesis is obtained by the addition of colors one to another in the form of light rather than as colorants. This color addition may take place (1) by the simultaneous projection of two or more (usually three) color images onto a screen, (2) by the projection of the color images in rapid succession onto a screen or (3) by viewing minutely divided juxtaposed color images.

In the case of a three-color process, three-color records are made from the subject recording, in terms of silver densities, the relative amounts of red, green, and blue present in various areas of the subject.

When the additive synthesis is to be made by simultaneous projection, positives are made from the color separation negatives and projected with a triple lantern onto a screen through red, green, and blue filters. The registered color images give all colors of the subject due to simple color addition, red plus green making yellow, red plus blue appearing magenta, etc.

When the additive synthesis is made by successive viewing, the same three-color images must be flashed onto the screen in such rapid succession that the individual red, green, and blue images are not apparent. Simple

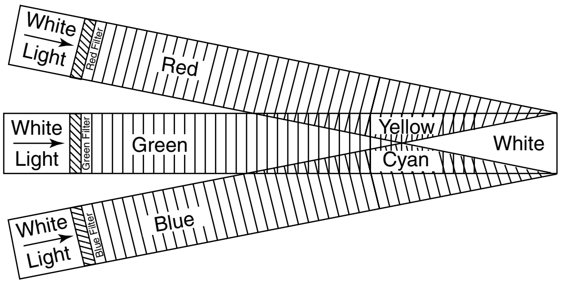
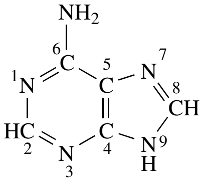


Fig. 1. Mechanism of color addition

color addition is again obtained but this time use is made of the persistence of vision to "mix" the colors. See Fig. 1.

The third type of additive synthesis makes use of the fact that small dots of different colors, when viewed from such a distance that they are no longer individually visible, form a single color by simple color addition. The three-color images in this type of process are generally side by side in the space normally occupied by a single image. The red record image will be composed of a number of red dots or markings of differing density which, in total, will compose the red record image. Alongside the red markings will be green and blue markings, without any overlapping. When viewed at such a distance that the colored markings are at, or below, the limit of visual resolution, the color sensation from any given area will be the integrated color of the markings comprising the area—an additive color mixture.

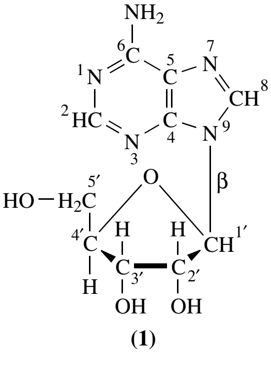
ADENINE. [CAS: 73-24-5]. A prominent member of the family of naturally occurring purines (see Structure 1). Adenine occurs not only in ribonucleic acids (RNA), and deoxyribonucleic acids (DNA), but in nucleosides, such as adenosine, and nucleotides, such as adenylic acid, which may be linked with enzymatic functions quite apart from nucleic acids. Adenine, in the form of its ribonucleotide, is produced in mammals and fowls endogenously from smaller molecules and no nutritional essentiality is ascribed to it. In the nucleosides, nucleotides, and nucleic acids, the attachment or the sugar moiety is at position 9.



(1)

The purines and pyrimidines absorb ultraviolet light readily, with absorption peaks at characteristic frequencies. This has aided in their identification and quantitative determination.

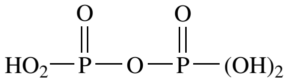
ADENOSINE. [CAS: 58-61-7]. An important nucleoside composed of adenine and ribose. White, crystalline, odorless powder, mild, saline, or bitter taste, Mp 229C, quite soluble in hot water, practically insoluble in alcohol. Formed by isolation following hydrolysis of yeast nucleic acid. The upper portion of Structure 1 represents the adenine moiety, and the lower portion of the pentose, D-ribose.



(1)

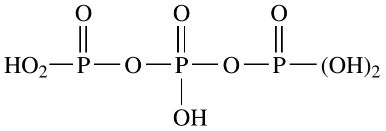
ADENOSINE DI-AND TRIPHOSPHATE. See **Carbohydrates**; **Phosphorylation (Oxidative)**; **Phosphorylation (Photosynthetic)**.

ADENOSINE PHOSPHATES. The adenosine phosphates include *adenylic acid* (adenosine monophosphate, AMP) in which adenosine is esterified with phosphoric acid at the 5′-position; *adenosine diphosphate* (ADP) in which esterification at the same position is with pyrophosphoric acid,



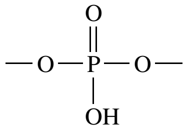
$$\mathrm{HO_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(OH)_2}$$

and *adenosine triphosphate* (ATP) in which three phosphate residues



$$\mathrm{HO_2{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}O{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{P}{-}(OH)_2}$$

are attached at the 5′-position. Adenosine-3′-phosphate is an isomer of adenylic acid, and adenosine-2′, 3′-phosphate is esterified in two positions with the same molecules of phosphoric acid and contains the radical.



$$\mathrm{{-}O{-}\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}{-}O{-}}$$

ADHESIVES. An *adhesive* is a material capable of holding together solid materials by means of surface attachment. *Adhesion* is the physical attraction of the surface of one material for the surface of another. An *adherend* is the solid material to which the adhesive adheres and the *adhesive bond* or *adhesive joint* is the assembly made by joining adherends together by means of an adhesive. *Practical adhesion* is the physical strength of an adhesive bond. It primarily depends on the forces of adhesion, but its magnitude is determined by the physical properties of the adhesive and the adherend, as well as the engineering of the adhesive bond.

The *interphase* is the volume of material in which the properties of one substance gradually change into the properties of another. The interphase is useful for describing the properties of an adhesive bond. The *interface*, contained within the interphase, is the plane of contact between the surface of one material and the surface of another. Except in certain special cases, the interface is imaginary. It is useful in describing surface energetics.

Theories of Adhesion

There is no unifying theory of adhesion describing the relationship between practical adhesion and the basic intermolecular and interatomic interactions which take place between the adhesive and the adherend either at the interface or within the interphase. The existing adhesion theories are, for the most part, rationalizations of observed phenomena, although in some cases, predictions regarding the relative ranking of practical adhesion can actually be made.

Diffusion Theory. The diffusion theory of adhesion is mostly applied to polymers. It assumes mutual solubility of the adherend and adhesive to form an interphase.

Electrostatic Theory. The basis of the electrostatic theory of adhesion is the differences in the electronegativities of adhering materials which leads to a transfer of charge between the materials in contact. The attraction of the charges is considered the source of adhesion.

Surface Energetics and Wettability Theory. The surface energetics and wettability theory of adhesion is concerned with the effect of intermolecular and interatomic forces on the surface energies of the adhesive and the adherend and the interfacial energy between the two.

Mechanical Interlocking Theory. A practical adhesion can be enhanced if the adhesive is applied to a surface which is microscopically rough.

Guidelines for Good Adhesion. The various adhesion theories can be used to formulate guidelines for good adhesion:

1. An adhesive should possess a liquid surface tension that is less than the critical wetting tension of the adherend's surface.

2. The adherend should be mechanically rough enough so that the asperities on the surface are on the order of, or less than, one micrometer in size.
3. The adhesive's viscosity and application conditions should be such that the asperities on the adherend's surface are completely wetted.
4. If an adverse environment is expected, covalent bonding capabilities at the interface should be provided.

For good adhesion, the adhesive and the adherend should, if possible, display mutual solubility to the extent that both diffuse into one another, providing an interphasal zone.

Advantages and Disadvantages of Using Adhesives

Adhesive Advantages. In comparison to other methods of joining, adhesives provide several advantages. First, a properly applied adhesive provides a joint having a more uniform stress distribution under load than a mechanical fastener which requires a hole in the adherend. Second, adhesives provide the ability to bond dissimilar materials such as metals without problems such as galvanic corrosion. Third, using an adhesive to make an assembly increases fatigue resistance. Fourth, adhesive joints can be made of heat- or shock-sensitive materials. Fifth, adhesive joining can bond and seal simultaneously. Sixth, use of an adhesive to form an assembly usually results in a weight reduction in comparison to mechanical fasteners since adhesives, for the most part, have densities which are substantially less than that of metals.

Adhesive Disadvantages. There are some limitations in using adhesives to form assemblies. The major limitation is that the adhesive joint is formed by means of surface attachment and is, therefore, sensitive to the substrate surface condition. Another limitation of adhesive bonding is the lack of a nondestructive quality control procedure. Finally, adhesive joining is still somewhat limited because most designers of assemblies are simply not familiar with the engineering characteristics of adhesives.

Mechanical Tests of Adhesive Bonds

The three principal forces to which adhesive bonds are subjected are a shear force in which one adherend is forced past the other, peeling in which at least one of the adherends is flexible enough to be bent away from the adhesive bond, and cleavage force. The cleavage force is very similar to the peeling force, but the former applies when the adherends are nondeformable and the latter when the adherends are deformable. Appropriate mechanical testing of these forces are used. Fracture mechanics tests are also typically used for structural adhesives.

Table 1 provides the approximate load-bearing capabilities of various adhesive types. Because the load-bearing capabilities of an adhesive are dependent upon the adherend material, the loading rate, temperature, and design of the adhesive joint, wide ranges of performance are listed.

Chemistry and Uses of Adhesives

Structural Adhesives. A structural adhesive is a resin system, usually a thermoset, that is used to bond high strength materials in such a way that the bonded joint is able to bear a load in excess of 6.9 MPa (1000 psi) at room temperature. Structural adhesives are the strongest form of adhesive and are meant to hold loads permanently. They exist in a number of forms. The most common form is the two-part adhesive, widely available as a consumer product. The next most familiar is that which is obtained as a room temperature curing liquid. Less common are primer—liquid adhesive combinations which cure at room temperature. Structural adhesive pastes which cure at 120°C are widely available in the industrial market.

TABLE 1. LOAD-BEARING CAPABILITIES OF ADHESIVES[a]

Adhesive type	Shear load, MPa[b]	Peel load, N/m[c]
pressure sensitive	0.005–0.02[d]	300–600
rubber based	0.3–7	1000–7000
emulsion	10–14	
hot melt	1–15	1000–5000
natural product (structural)	10–14	
polyurethane	6–17	2000–10,000
acrylic	6–20	900–6000
epoxy	14–50	700–18,000
phenolic	14–35	700–9000
polyimide	13–17	350–1760

[a] Load bearing capabilities are dependent upon the adherend, joint design, rate of loading, and temperature. Values given represent the type of adherends normally used at room temperature. Lap shear values approximate those obtainable from an overlap of 3.2 cm^2.

[b] To convert from MPa to psi, multiply by 145.

[c] To convert from N/m to ppi, divide by 175.

[d] Pressure-sensitive adhesives normally are rated in terms of shear holding power, i.e., time to fail in minutes under a constant load.

Structural adhesives are formulated from epoxy resins, phenolic resins, acrylic monomers and resins, high temperature-resistant resins (e.g., polyimides), and urethanes. Structural adhesive resins are often modified by elastomers.

Natural-product-based structural adhesives include protein-based adhesives, starch-based adhesives, and cellulosics.

Pressure-Sensitive Adhesives. A pressure-sensitive adhesive, a material which adheres with no more than applied finger pressure, is aggressively and permanently tacky. It requires no activation other than the finger pressure, exerts a strong holding force, and should be removable from a smooth surface without leaving a residue.

Applications and Formulation. Pressure-sensitive adhesives are most widely used in the form of adhesive tapes. The general formula for a pressure-sensitive adhesive includes an elastomeric polymer, a tackifying resin, any necessary fillers, various antioxidants and stabilizers, if needed, and cross-linking agents.

Hot-Melt Adhesives. Hot-melt adhesives are 100% nonvolatile thermoplastic materials that can be heated to a melt and then applied as a liquid to an adherend. The bond is formed when the adhesive resolidifies. The oldest example of a hot-melt adhesive is sealing wax.

Solvent- and Emulsion-Based Adhesives. *Solvent-Based Adhesives.* Solvent-based adhesives, as the name implies, are materials that are formed by solution of a high molecular weight polymer in an appropriate solvent. Solvent-based adhesives are usually elastomer-based and formulated in a manner similar to pressure-sensitive adhesives.

Emulsion Adhesives. The most widely used emulsion-based adhesive is that based upon poly(vinyl acetate)–poly(vinyl alcohol) copolymers formed by free-radical polymerization in an emulsion system. Poly(vinyl alcohol) is typically formed by hydrolysis of the poly(vinyl acetate). This is also known as "white glue."

Economic Aspects

Although the manufacture and sale of adhesives is a worldwide enterprise, the adhesives business can be characterized as a fragmented industry. The 1987 Census of Manufacturers obtained reports from 712 companies in the United States, each of which considers itself to be in the adhesives or sealants business; only 275 of these companies had more than 20 employees. Phenolics, poly(vinyl acetate) adhesives, rubber cements, and hot-melt adhesives are the leading products in terms of monetary value. These products are used primarily in the wood, paper, and packaging industries. The annual growth rate of the adhesives market is 2.3%, and individual segments of the market are expected to grow faster than this rate.

An excellent review of "Adhesive Bonding" is contained in the *Modern Plastic Encyclopedia*, issued annually by Modern Plastics, Pittsfield, Massachusetts.

For further information, refer to Case Western Reserve University in Cleveland, Ohio, which maintains a fundamental research center for adhesives and coatings. http://www.cwru.edu/cse/eche/

ALPHONSUS V. POCIUS
The 3M Company

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ADIABATIC PROCESS. Any thermodynamic process, reversible or irreversible, which takes place in a system without the exchange of heat with the surroundings. When the process is also reversible, it is called *isentropic*, because then the entropy of the system remains constant at every step of the process. (In older usage, isentropic processes were called simply adiabatic, or quasistatic adiabatic; the distinction between adiabatic and isentropic processes was not always sharply drawn.)

When a closed system undergoes an adiabatic process without performing work (*unresisted expansion*), its internal energy remains constant whenever the system is allowed to reach thermal equilibrium. Such a process is necessarily irreversible. At each successive state of equilibrium, the entropy of the system S_i, has a higher value than the initial entropy, S_0. Example: When a gas at pressure p_0, temperature T_0, occupying a volume V_0 (see Fig. 1) is allowed to expand progressively into volumes $V_1 = V_0 + \Delta V$, etc., by withdrawing slides 1, 2, etc., one after another, it undergoes such a process if it is enclosed in an adiabatic container. After each withdrawal of a slide, the irreversibility of the process causes the system to depart from equilibrium; equilibrium sets in after a sufficiently long waiting period. At each successive state of equilibrium $U_1 = U_2 = \cdots = U_0$, but $S_0 < S_1 < S_2$, etc.

When an open system in steady flow undergoes an adiabatic process without performing external work, the enthalpy of the system regains its initial value at each equilibrium state, and the entropy increases as before. Example: Successive, *slow* expansions through porous plugs $P_1, P_2 \cdots$ (Fig. 2), when we have

$$H_1 = H_2 = \cdots = H_0$$

but

$$S_0 < S_1 < S_2, \text{ etc.}$$

This process is also necessarily irreversible.

A closed system cannot perform an isentropic process without performing work. Example (Fig. 3): A quantity of gas enclosed by an ideal, frictionless, adiabatic piston in an adiabatic cylinder is maintained at a pressure p by a suitable ideal mechanism, so that $Gl = pA$ (A being the area of piston). When the weight G is increased (or decreased) by an infinitesimal amount dG, the gas will undergo an isentropic compression (or expansion). In this case,

$$S = \text{constant}, \quad dS = 0$$

at any stage of the process, but

$$U \neq \text{constant}, \quad H \neq \text{constant}$$

During an isentropic process of a closed system between state 1 and 2, the change in internal energy equals *minus* the work done between the two states, or

$$U_2 - U_1 = -W_{12}$$

work is done "at the expense" of the internal energy.

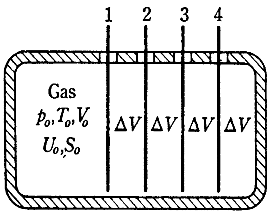

Fig. 1. Successive adiabatic expansions of gas by withdrawing slides.

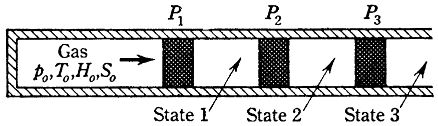

Fig. 2. Successive, slow adiabatic expansions of gas through porous plugs.

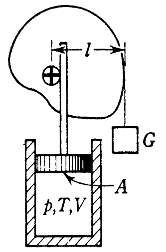

Fig. 3. Isentropic compression (or expansion) in cylinder.

ADIPIC ACID. [CAS: 124-04-9]. Adipic acid, hexanedioic acid, 1,4-butanedicarboxylic acid, mol wt 146.14, $HOOCCH_2CH_2CH_2CH_2COOH$, is a white crystalline solid with a melting point of about 152°C. Little of this dicarboxylic acid occurs naturally, but it is produced on a very large scale at several locations around the world. The majority of this material is used in the manufacture of nylon-6,6 polyamide, which is prepared by reaction with 1,6-hexanediamine.

Chemical and Physical Properties

Adipic acid is a colorless, odorless, sour-tasting crystalline solid. Its fundamental chemical and physical properties are listed in Table 1.

Chemical Reactions

Adipic acid undergoes the usual reactions of carboxylic acids, including esterification, amidation, reduction, halogenation, salt formation, and dehydration. Because of its bifunctional nature, it also undergoes several industrially significant polymerization reactions.

Manufacture and Processing

Adipic acid historically has been manufactured predominantly from cyclohexane and, to a lesser extent, phenol. During the 1970s and 1980s, however, much research has been directed to alternative feedstocks, especially butadiene and cyclohexene, as dictated by shifts in hydrocarbon markets. All current industrial processes use nitric acid in the final oxidation stage. Growing concern with air quality may exert further pressure for alternative routes as manufacturers seek to avoid NO_x abatement costs, a necessary part of processes that use nitric acid.

Since adipic acid has been produced in commercial quantities for almost 50 years, it is not surprising that many variations and improvements have been made to the basic cyclohexane process. In general, however, the commercially important processes still employ two major reaction stages. The first reaction stage is the production of the intermediates cyclohexanone and cyclohexanol, usually abbreviated as KA, KA oil, ol-one, or anone-anol. The KA (ketone, alcohol), after separation from unreacted cyclohexane (which is recycled) and reaction by-products, is

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF ADIPIC ACID

Property	Value
molecular formula	$C_6H_{10}O_4$
molecular weight	146.14
melting point, °C	152.1 ± 0.3
specific gravity	1.344 at 18°C (sol)
	1.07 at 170°C (liq)
vapor pressure, Pa[a]	
solid at °C	
18.5	9.7
47.0	38.0
liquid at °C	
205.5	1300
244.5	6700
specific heat, kJ/kg·K[b]	1.590 (solid state)
	2.253 (liquid state)
	1.680 (vapor, 300°C)
heat of fusion, kJ/kg[b]	115
melt viscosity, mPa·s (= cP)	4.54 at 160°C
heat of combustion, kJ/mol[b]	2800

[a] To convert Pa to mm Hg, divide by 133.3.

[b] To convert J to cal, divide by 4.184.

then converted to adipic acid by oxidation with nitric acid. An important alternative to this use of KA is its use as an intermediate in the manufacture of caprolactam, the monomer for production of nylon-6. The latter use of KA predominates by a substantial margin on a worldwide basis, but not in the United States.

Storage, Handling, and Shipping

When dispersed as a dust, adipic acid is subject to normal dust explosion hazards. The material is an irritant, especially upon contact with the mucous membranes. Thus protective goggles or face shields should be worn when handling the material.

The material should be stored in corrosion-resistant containers, away from alkaline or strong oxidizing materials.

Economic Aspects

Adipic acid is a very large-volume organic chemical. It is one of the top 50 chemicals produced in the United States in terms of volume. Demand is highly cyclic, reflecting the automotive and housing markets especially. Prices usually follow the variability in crude oil prices. Adipic acid for nylon takes about 60% of U.S. cyclohexane production; the remainder goes to caprolactam for nylon-6, export, and miscellaneous uses.

Toxicity, Safety, and Industrial Hygiene

Adipic acid is relatively nontoxic; no OSHA PEL or NIOSH REL have been established for the material.

Darwin D. Davis
Donald R. Kemp
E.I. du Pont de Nemours & Co., Inc.

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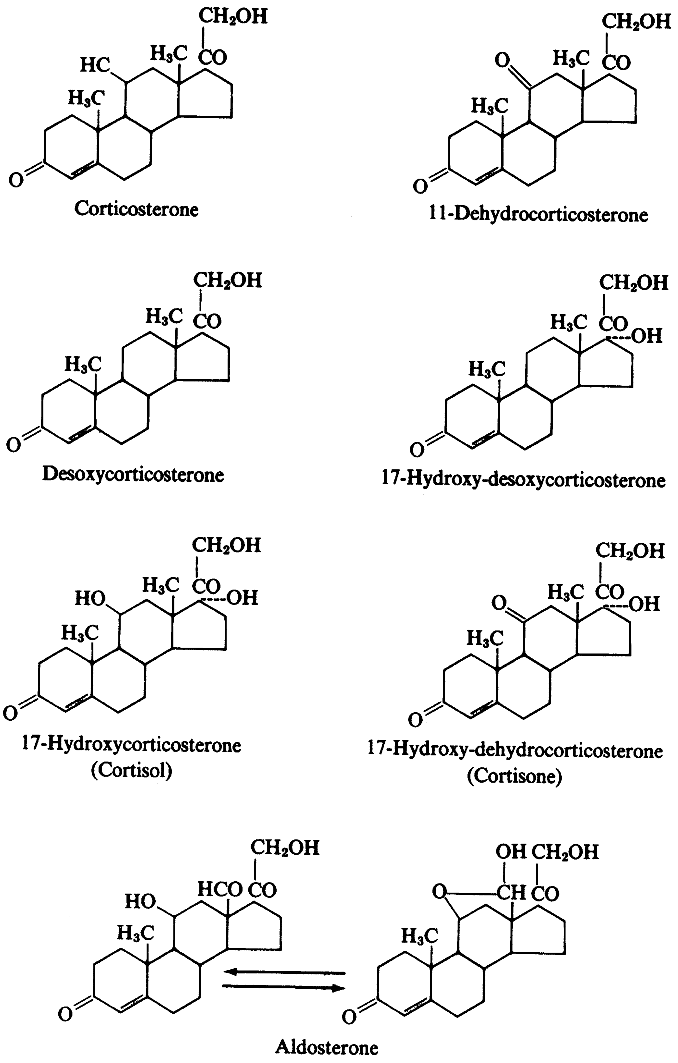
ADRENAL CORTICAL HORMONES. The hormones elaborated by the adrenal cortex are steroidal derivatives of cyclopentanoperhydrophenanthrene related to the sex hormones. The structural formulas of the important members of this group are shown in Fig. 1. With the exception of *aldosterone*, the compounds may be considered derivatives of *corticosterone*, the first of the series to be identified and named. The C_{21} steroids derived from the adrenal cortex and their metabolities are designated collectively as *corticosteroids*. They belong to two principal groups; (1) those processing an O or OH substituent at C_{11} (*corticosterone*) and an OH group at C_{17} (*cortisone* and *cortisol*) exert their chief action on organic metabolism and are designated as *glucocorticoids*; (2) those lacking the oxygenated group at C_{17} (*desoxycorticosterone* and *aldosterone*) act primarily on electrolyte and water metabolism and are designated as *mineralocorticoids*. In humans, the chief glucocorticoid is *cortisol*. The chief mineralocorticoid is *aldosterone*.

The *glucocorticoids* are involved in organic metabolism and in the organism's response to stress. They accelerate the rate of catabolism (destructive metabolism) and inhibit the rate of anabolism (constructive metabolism) of protein. They also reduce the utilization of carbohydrate and increase the rate of gluconeogenesis (formation of glucose) from protein. They also exert a lipogenic as well as lipolytic action, potentiating the release of fatty acids from adipose tissue. In addition to these effects on the organic metabolism of the basic foodstuffs, the glucocorticoids affect the body's allergic, immune, inflammatory, antibody, anamnestic, and general responses of the organism to environmental disturbances. It is these reactions which are the basis for the wide use of the corticosteroids therapeutically. See also **Immune System and Immunochemistry**.

Aldosterone exerts its main action in controlling the water and electrolyte metabolism. Its presence is essential for the reabsorption of sodium by the renal tube, and it is the loss of salt and water which is responsible for the acute manifestations of adrenocortical insufficiency. The action of aldosterone is not limited to the kidney, but is manifested on the cells generally, this hormone affecting the distribution of sodium, potassium, water, and hydrogen ions between the cellular and extracellular fluids independently of its action on the kidney.



Corticosterone

11-Dehydrocorticosterone

Desoxycorticosterone

17-Hydroxy-desoxycorticosterone

17-Hydroxycorticosterone
(Cortisol)

17-Hydroxy-dehydrocorticosterone
(Cortisone)

Aldosterone

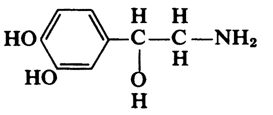
Fig. 1. Adrenal cortical hormones

The differentiation in action of the glucocorticoids and the mineralocorticoids is not an absolute one. Aldosterone is about 500 times as effective as cortisol in its salt and water retaining activity, but is one-third as effective in its capacity to restore liver glycogen in the adrenalectomized animal. Cortisol in large doses, on the other hand, exerts a water and salt retaining action. Corticosterone is less active than cortisol as a glucocorticoid, but exerts a more pronounced mineralocorticoid action than does the latter. See also **Steroids**.

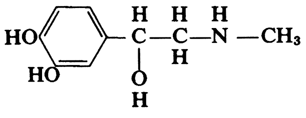
In addition to the aforementioned corticosteroidal hormones, the adrenal glands produce several oxysteroids and small amounts of testosterone and other androgens, estrogens, progesterone, and their metabolites.

ADRENAL MEDULLA HORMONES. *Adrenaline (epinephrine)* and its immediate biological precursor *noradrenaline* (*norepinephrine*, levarternol) are the principal hormones of the adult adrenal medulla. See Fig.1. Some of the physiological effects produced by adrenaline are: contraction of the dilator muscle of the pupil of the eye (*mydriasis*); relaxation of the smooth muscle of the bronchi; constriction of most small blood vessels; dilation of some blood vessels, notably those in skeletal muscle; increase in heart rate and force of ventricular contraction; relaxation of the smooth muscle of the intestinal tract; and either contraction or relaxation, or both, of uterine smooth muscle. Electrical stimulation of appropriate sympathetic (*adrenergic*) nerves can produce all the aforementioned effects with exception of vasodilation in skeletal muscle.

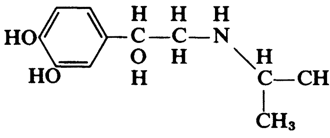
Noradrenaline, when administered, produces the same general effects as adrenaline, but is less potent. Isoproternol, a synthetic analogue of noradrenaline, is more potent than adrenaline in relaxing some smooth muscle, producing vasodilation and increasing the rate and force of cardiac contraction.



Noradrenaline



Adrenaline



Isoproterenol (Synthetic)

Fig. 1. Adrenal medula hormones

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ADSORPTION. Adsorption is the term used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. This is a fundamental property of matter, having its origin in the attractive forces between molecules. The force field creates a region of low potential energy near the solid surface and, as a result, the molecular density close to the surface is generally greater than in the bulk gas. Furthermore, and perhaps more importantly, in a multicomponent system the composition of this surface layer generally differs from that of the bulk gas since the surface adsorbs the various components with different affinities. Adsorption may also occur from the liquid phase and is accompanied by a similar change in composition, although, in this case, there is generally little difference in molecular density between the adsorbed and fluid phases.

The enhanced concentration at the surface accounts, in part, for the catalytic activity shown by many solid surfaces, and it is also the basis of the application of adsorbents for low pressure storage of permanent gases such as methane. However, most of the important applications of adsorption depend on the selectivity, i.e., the difference in the affinity of the surface for different components. As a result of this selectivity, adsorption offers, at least in principle, a relatively straight-forward means of purification (removal of an undesirable trace component from a fluid mixture) and a potentially useful means of bulk separation.

Fundamental Principles

Forces of Adsorption. Adsorption may be classified as chemisorption or physical adsorption, depending on the nature of the surface forces. In physical adsorption the forces are relatively weak, involving mainly van der Waals (induced dipole–induced dipole) interactions, supplemented in many cases by electrostatic contributions from field–dipole or field–gradient–quadrupole interactions. By contrast, in chemisorption there is significant electron transfer, equivalent to the formation of a chemical bond between the sorbate and the solid surface. Such interactions are both stronger and more specific than the forces of physical adsorption and are obviously limited to monolayer coverage.

Selectivity. Selectivity in a physical adsorption system may depend on differences in either equilibrium or kinetics, but the great majority of adsorption separation processes depend on equilibrium-based selectivity. Significant kinetic selectivity is, in general, restricted to molecular sieve adsorbents—carbon molecular sieves, zeolites, or zeolite analogues.

Hydrophilic and Hydrophobic Surfaces. Polar adsorbents such as most zeolites, silica gel, or activated alumina adsorb water (a small polar molecule) more strongly than they adsorb organic species, and, as a result, such adsorbents are commonly called hydrophilic. In contrast, on a nonpolar surface where there is no electrostatic interaction, water is held only very weakly and is easily displaced by organics. Such adsorbents, which are the only practical choice for adsorption of organics from aqueous solutions, are termed hydrophobic.

Capillary Condensation. In a porous adsorbent the region of multilayer physical adsorption merges gradually with the capillary condensation regime, leading to upward curvature of the equilibrium isotherm at higher relative pressure. In the capillary condensation region the intrinsic selectivity of the adsorbent is lost.

Practical Adsorbents

To achieve a significant adsorptive capacity an adsorbent must have a high specific area, which implies a highly porous structure with very small micropores. Such microporous solids can be produced in several different ways. Adsorbents such as silica gel and activated alumina are made by precipitation of colloidal particles, followed by dehydration. Carbon adsorbents are prepared by controlled burn-out of carbonaceous materials such as coal, lignite, and coconut shells. The crystalline adsorbents (zeolite and zeolite analogues) are different in that the dimensions of the micropores are determined by the crystal structure and there is therefore virtually no distribution of micropore size. Although structurally very different from the crystalline adsorbents, carbon molecular sieves also have a very narrow distribution of pore size. The adsorptive properties depend on the pore size and the pore size distribution as well as on the nature of the solid surface.

Adsorption Equilibrium

Henry's Law. Like any other phase equilibrium, the distribution of a sorbate between fluid and adsorbed phases is governed by the principles of thermodynamics. Equilibrium data are commonly reported in the form of an isotherm, which is a diagram showing the variation of the equilibrium adsorbed-phase concentration or loading with the fluid-phase concentration or partial pressure at a fixed temperature. In general, for physical adsorption on a homogeneous surface at sufficiently low concentrations, the isotherm should approach a linear form, and the limiting slope in the low concentration region is commonly known as the Henry's law constant. The Henry constant is a thermodynamic equilibrium constant and the temperature dependence therefore follows the usual van't Hoff equation:

$$\lim p \to 0 \left(\frac{\delta q}{\delta p}\right) T \equiv K' = K'_0 e^{-\Delta H_0/\mathrm{RT}} \qquad (1)$$

in which $-\Delta H_0$ is the limiting heat of adsorption at zero coverage. Since adsorption, particularly from the vapor phase, is usually exothermic, $-\Delta H_0$ is a positive quantity and K' therefore decreases with increasing temperature.

Henry's law corresponds physically to the situation in which the adsorbed phase is so dilute that there is neither competition for surface sites nor any significant interaction between adsorbed molecules. At higher concentrations both of these effects become important and the form of the isotherm becomes more complex. The isotherms have been classified into five different types (Fig. 1). Isotherms for a microporous adsorbent are generally of type I; the more complex forms are associated with multilayer adsorption and capillary condensation.

Langmuir Isotherm. Type I isotherms are commonly represented by the ideal Langmuir model:

$$\frac{q}{q_s} = \frac{bp}{1 + bp} \qquad (2)$$

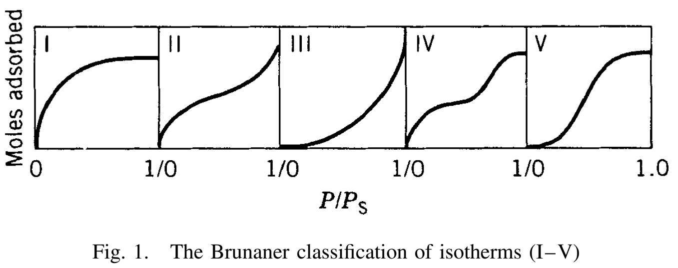

Fig. 1. The Brunaner classification of isotherms (I–V)

where q_s is the saturation limit and b is an equilibrium constant which is directly related to the Henry constant ($K' = bq_s$).

Freundlich Isotherm. The isotherms for some systems, notably hydrocarbons on activated carbon, conform more closely to the Freundlich equation:

$$q = bp^{1/n} (n > 1.0) \tag{3}$$

Adsorption of Mixtures. The Langmuir model can be easily extended to binary or multicomponent systems:

$$\frac{q_1}{q_{s1}} = \frac{b_1 p_1}{1 + b_1 p_1 + b_2 p_2 + \cdots}; \frac{q_2}{q_{s2}} = \frac{b_2 p_2}{1 + b_1 p_1 + b_2 p_2; + \cdots} \tag{4}$$

Thermodynamic consistency requires $q_{s1} = q_{s2}$, but this requirement can cause difficulties when attempts are made to correlate data for sorbates of very different molecular size. For such systems it is common practice to ignore this requirement, thereby introducing an additional model parameter. This facilitates data fitting but it must be recognized that the equations are then being used purely as a convenient empirical form with no theoretical foundation.

Ideal Adsorbed Solution Theory. Perhaps the most successful general approach to the prediction of multicomponent equilibria from single-component isotherm data is ideal adsorbed solution theory. In essence, the theory is based on the assumption that the adsorbed phase is thermodynamically ideal in the sense that the equilibrium pressure for each component is simply the product of its mole fraction in the adsorbed phase and the equilibrium pressure for the pure component *at the same spreading pressure*. The theoretical basis for this assumption and the details of the calculations required to predict the mixture isotherm are given in standard texts on adsorption. Whereas the theory has been shown to work well for several systems, notably for mixtures of hydrocarbons on carbon adsorbents, there are a number of systems which do not obey this model. Azeotrope formation and selectivity reversal, which are observed quite commonly in real systems, are not consistent with an ideal adsorbed phase and there is no way of knowing *a priori* whether or not a given system will show ideal behavior.

Adsorption Kinetics

Intrinsic Kinetics. Chemisorption may be regarded as a chemical reaction between the sorbate and the solid surface, and, as such, it is an activated process for which the rate constant (k) follows the familiar Arrhenius rate law:

$$k = k_0 e^{-E/RT} \tag{5}$$

Depending on the temperature and the activation energy (E), the rate constant may vary over many orders of magnitude.

In practice the kinetics are usually more complex than might be expected on this basis, since the activation energy generally varies with surface coverage as a result of energetic heterogeneity and/or sorbate—sorbate interaction. As a result, the adsorption rate is commonly given by the Elovich equation:

$$q = \frac{1}{k'} \ln(1 + k''t) \tag{6}$$

where k' and k'' are temperature-dependent constants.

In contrast, physical adsorption is a very rapid process, so the rate is always controlled by mass transfer resistance rather than by the intrinsic adsorption kinetics. However, under certain conditions the combination of a diffusion-controlled process with an adsorption equilibrium constant that varies according to equation 1 can give the appearance of activated adsorption.

A porous adsorbent in contact with a fluid phase offers at least two and often three distinct resistances to mass transfer: external film resistance and intraparticle diffusional resistance. When the pore size distribution has a well-defined bimodal form, the latter may be divided into macropore and micropore diffusional resistances. Depending on the particular system and the conditions, any one of these resistances may be dominant, or the overall rate of mass transfer may be determined by the combined effects of more than one resistance. The magnitude of the intraparticle diffusional resistances, or any surface resistance to mass transfer, can be conveniently determined by measuring the adsorption or desorption rate, under controlled conditions, in a batch system.

Adsorption Column Dynamics

In most adsorption processes the adsorbent is contacted with fluid in a packed bed. An understanding of the dynamic behavior of such systems is therefore needed for rational process design and optimization. What is required is a mathematical model which allows the effluent concentration to be predicted for any defined change in the feed concentration or flow rate to the bed. The flow pattern can generally be represented adequately by the axial dispersed plug-flow model, according to which a mass balance for an element of the column yields, for the basic differential equation governing the dynamic behavior,

$$-D_L \frac{\delta^2 c_i}{\delta z^2} + \frac{\delta}{\delta z}(v c_i) + \frac{\delta c_i}{\delta t} + \left(\frac{1-\varepsilon}{\varepsilon}\right) \frac{\delta \overline{q}_i}{\delta t} = 0 \tag{7}$$

The term $\delta \overline{q}_i / \delta t$ represents the overall rate of mass transfer for component i (at time t and distance z) averaged over a particle. This is governed by a mass transfer rate expression which may be thought of as a general functional relationship of the form

$$\frac{\delta \overline{q}}{\delta t} = f(c_i, c_j, \cdots q_i, q_j, \cdots) \tag{8}$$

This rate equation must satisfy the boundary conditions imposed by the equilibrium isotherm and it must be thermodynamically consistent so that the mass transfer rate falls to zero at equilibrium.

Equilibrium Theory. The general features of the dynamic behavior may be understood without recourse to detailed calculations since the overall pattern of the response is governed by the form of the equilibrium relationship rather than by kinetics. If the equilibrium isotherm is of "favorable" form (i.e., slope decreasing with increasing concentration as in Figure 1,I) the concentration front, for adsorption, will assume the form of a travelling shock wave, whereas for desorption the front will assume the form of a simple wave which spreads as it propagates through the column.

Constant Pattern Behavior. In a real system the finite resistance to mass transfer and axial mixing in the column lead to departures from the idealized response predicted by equilibrium theory. In the case of a favorable isotherm the shock wave solution is replaced by a constant pattern solution. The concentration profile spreads in the initial region until a stable situation is reached in which the mass transfer rate is the same at all points along the wave front and exactly matches the shock velocity. In this situation the fluid-phase and adsorbed-phase profiles become coincident. This represents a stable situation and the profile propagates without further change in shape—hence the term constant pattern.

Length of Unused Bed. The constant pattern approximation provides the basis for a very useful and widely used design method based on the concept of the length of unused bed (LUB). In the design of a typical adsorption process the basic problem is to estimate the size of the absorber bed needed to remove a certain quantity of the adsorbable species from the feed stream, subject to a specified limit (c') on the effluent concentration. The length of unused bed, which measures the capacity of the adsorber which is lost as a result of the spread of the concentration profile, is defined by

$$\text{LUB} = (1 - q'/q_o)L = (1 - t'/\overline{t})L \tag{9}$$

where q' is the capacity at the break time t' and $\overline{t}$ is the stoichiometric time (see Fig. 2). The values of t', $\overline{t}$, and hence the LUB are easily determined from an experimental breakthrough curve since, by overall mass balance:

$$\overline{t} = \frac{L}{v}\left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{q_0}{c_0}\right)\right] = \int_{\infty}^{0} \left(1 - \frac{c}{c_0}\right) dt \tag{10}$$

$$t' = \frac{L}{v}\left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{q'}{c_0}\right)\right] = \int_{L'}^{0} \left(1 - \frac{c}{c_0}\right) dt \tag{11}$$

The length of column needed for a particular duty can then be found simply by adding the LUB to the length calculated from equilibrium considerations, assuming a shock concentration front.

Proportionate Pattern Behavior. If the isotherm is unfavorable (as in Fig. 1,III), the stable dynamic situation leading to constant pattern behavior can never be achieved. The equilibrium adsorbed-phase concentration then lies above rather than below the actual adsorbed-phase profile. As the mass transfer zone progresses through the column it broadens, but the limiting situation, which is approached in a long column, is simply local equilibrium at all points ($c = c^*$) and the profile therefore continues to

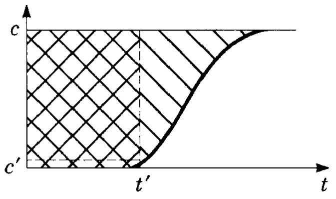

Fig. 2. Sketch of breakthrough curve showing break time t' and the method of calculation of the stoichiometric time $\bar{t}$ and LUB. ⊠ = the integral of equation 10; ▧ = integral of equation 11.

spread in proportion to the distance traveled. This difference in behavior is important since the LUB approach to design is clearly inapplicable under these conditions.

Adsorption Chromatography. In a linear multicomponent system (several sorbates at low concentration in an inert carrier) the wave velocity for each component depends on its adsorption equilibrium constant. Thus, if a pulse of the mixed sorbate is injected at the column inlet, the different species separate into bands which travel through the column at their characteristic velocities, and at the outlet of the column a sequence of peaks corresponding to the different species is detected. Measurement of the retention time ($\bar{t}$) under known flow conditions thus provides a simple means of determining the equilibrium constant (Henry constant).

In an ideal system with no axial mixing or mass-transfer resistance, the peaks for the various components propagate without spreading. However, in any real system the peak broadens as it propagates and the extent of this broadening is directly related to the mass transfer and axial dispersion characteristics of the column. Measurement of the peak broadening therefore provides a convenient way of measuring mass-transfer coefficients and intraparticle diffusivities.

Applications

The applications of adsorbents are many and varied. They may be classified as "regenerative" and "nonregenerative". Most process applications, in which the adsorbent is used as a means of purifying or separating the components of a gas or liquid mixture are regenerative. The process operates in a cyclic manner so that the adsorbent is alternately saturated and regenerated. Nonregenerative applications include the use of adsorbents in cigarette filters, in some water purification systems, as deodorants in health care products and as desiccants in storage, packaging and dual-pane windows.

Adsorption Separation and Purification Processes. Adsorption processes can be classified according to the flow system (cyclic batch or continuous countercurrent) and the method by which the adsorbent is regenerated. The two basic flow schemes are illustrated in Figure 3. The cyclic batch scheme is simpler but less efficient. It is generally used where selectivity is relatively high. Countercurrent or simulated countercurrent schemes are more expensive in initial cost and are generally used only for difficult separations in which selectivity is limited or mass-transfer resistance is high.

The three common methods of regeneration are thermal swing, pressure swing, and displacement. The main factors governing this choice are summarized in Table 1.

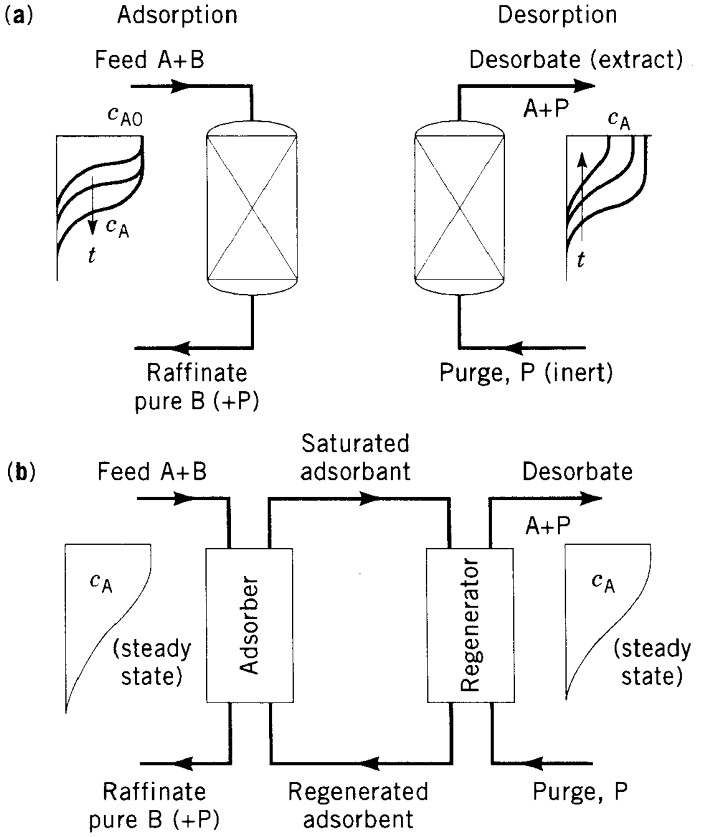

Fig. 3. The two basic modes of operation for an adsorption process: (**a**) cyclic batch system; (**b**) continuous countercurrent system with adsorbent recirculation.

Notation

b = Langmuir equilibrium constant
c = sorbate concentration in fluid phase
c_0 = initial value of c
D_L = axial dispersion coefficient
E = activation energy
$-\Delta H_0$ = limiting heat of adsorption
K' = Henry's law constant
K'_0 = preexponential factor
k = rate constant
k_0 = preexponential factor
k', k'' = constants in Elovich equation
L = bed length

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TABLE 1. FACTORS GOVERNING CHOICE OF REGENERATION METHOD

Method	Advantages	Disadvantages
thermal swing	good for strongly adsorbed species; small change in T gives large change in q^*	thermal aging of adsorbent
	desorbate may be recovered at high concentration	heat loss means inefficiency in energy usage
		unsuitable for rapid cycling, so adsorbent cannot be used with maximum efficiency
	gases and liquids	in liquid systems the latent heat of the interstitial liquid must be added
pressure swing	good where weakly adsorbed species is required at high purity	very low P may be required
		mechanical energy more expensive than heat
	rapid cycling—efficient use of adsorbent	desorbate recovered at low purity
displacement desorption	good for strongly held species	product separation and recovery needed (choice of desorbent is crucial)
	avoids risk of cracking reactions during regeneration	
	avoids thermal aging of adsorbent	

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ADSORPTION: GAS SEPARATION. Gas-phase adsorption is widely employed for the large-scale purification or bulk separation of air, natural gas, chemicals, and petrochemicals (Table 1). In these uses it is often a preferred alternative to the older unit operations of distillation and absorption.

An adsorbent attracts molecules from the gas, and the molecules become concentrated on the surface of the adsorbent and are removed from the gas phase. Many process concepts have been developed to allow the efficient contact of feed gas mixtures with adsorbents to carry out desired separations and to allow efficient regeneration of the adsorbent for subsequent reuse. In nonregenerative applications, the adsorbent is used only once and is not regenerated.

Most commercial adsorbents for gas-phase applications are employed in the form of pellets, beads, or other granular shapes, typically about 1.5 to 3.2 mm in diameter. Most commonly, these adsorbents are packed into fixed beds through which the gaseous feed mixtures are passed. Normally, the process is conducted in a cyclic manner. When the capacity of the bed is exhausted, the feed flow is stopped to terminate the loading step of the process, the bed is treated to remove the adsorbed molecules in a separate regeneration step, and the cycle is then repeated.

The growth in both variety and scale of gas-phase adsorption separation processes, particularly since 1970, is due in part to continuing discoveries of new porous, high surface-area adsorbent materials (particularly molecular sieve zeolites) and, especially, to improvements in the design and modification of adsorbents. These advances have encouraged parallel inventions of new process concepts. Increasingly, the development of new applications requires close cooperation in adsorbent design and process cycle development and optimization.

TABLE 1. COMMERCIAL ADSORPTION SEPARATIONS

Separation	Adsorbent
Gas bulk separations	
normal paraffins, isoparaffins, aromatics	zeolite
N_2/O_2	zeolite
O_2/N_2	carbon molecular sieve
CO, CH_4, CO_2, N_2, Ar, NH_3/H_2	zeolite, activated carbon
acetone/vent streams	activated carbon
C_2H_4/vent streams	activated carbon
H_2O/ethanol	zeolite
Gas purifications	
H_2O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc	silica, alumina, zeolite
CO_2/C_2H_4, natural gas, etc	zeolite
organics/vent streams	activated carbon, others
sulfur compounds/natural gas, hydrogen, liquified petroleum gas (LPG), etc	zeolite
solvents/air	activated carbon
odors/air	activated carbon
NO_x/N_2	zeolite
SO_2/vent streams	zeolite
Hg/chlor—alkali cell gas effluent	zeolite

Adsorption Principles

The design and manufacture of adsorbents for specific applications involves manipulation of the structure and chemistry of the adsorbent to provide greater attractive forces for one molecule compared to another, or, by adjusting the size of the pores, to control access to the adsorbent surface on the basis of molecular size. Adsorbent manufacturers have developed many technologies for these manipulations, but they are considered proprietary and are not openly communicated. Nevertheless, the broad principles are well known.

Adsorption Forces. Coulomb's law allows calculations of the electrostatic potential resulting from a charge distribution, and of the potential energy of interaction between different charge distributions. Various elaborate computations are possible to calculate the potential energy of interaction between point charges, distributed charges, etc.

Adsorption Selectivities. For a given adsorbent, the relative strength of adsorption of different adsorbate molecules depends on the relative magnitudes of the polarizability α, dipole moment μ, and quadrupole moment Q of each. Often, just the consideration of the values of α, μ, and Q allows accurate qualitative predictions to be made of the relative strengths of adsorption of given molecules on an adsorbent or of the best adsorbent type (polar or nonpolar) for a particular separation.

Heats of Adsorption. The integral heat of adsorption is the total heat released when the adsorbate loading is increased from zero to some final value at isothermal conditions. The differential heat of adsorption δH_{iso} is the incremental change in heat of adsorption with a differential change in adsorbate loading. This heat of adsorption δH_{iso} may be determined from the slopes of adsorption isosteres (lines of constant adsorbate loading) on graphs of ln P vs $1/T$ (Fig. 1) through the Clausius-Clapeyron relationship:

$$\frac{d \ln P}{d(1/T)} = -\frac{\delta H_{\text{iso}}}{R}$$

where R is the gas constant, P the adsorbate absolute pressure, and T the absolute temperature.

Isotherm Models. *Thermodynamically Consistent Isotherm Models.* These models include both the statistical thermodynamic models and the models that can be derived from an assumed equation of state for the adsorbed phase plus the thermodynamics of the adsorbed phase.

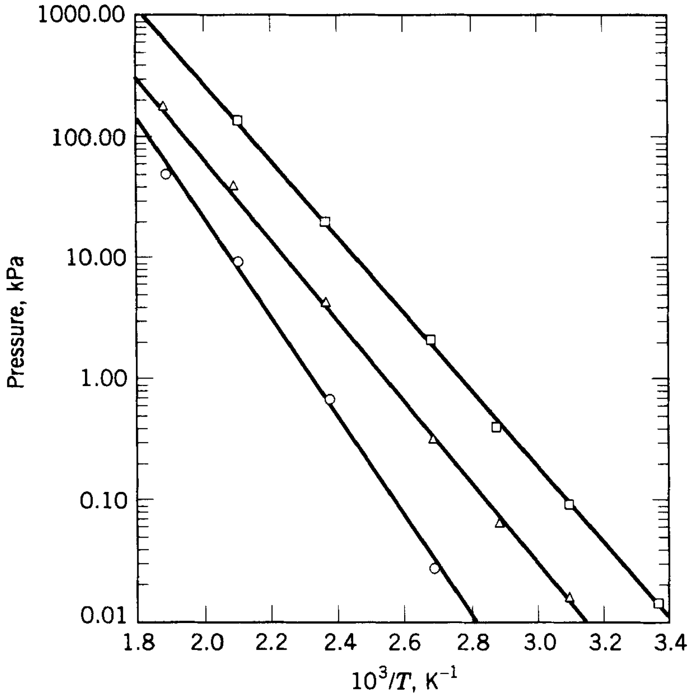

Fig. 1. Adsorption isosteres, water vapor on 4A (NaA) zeolite pellets. H_2O loading: □, 15 kg/100 kg zeolite; △, 10 kg/100 kg, ○, 5 kg/100 kg. To convert kPa to mm Hg, multiply by 7.5. Courtesy of Union Carbide

Statistical Thermodynamic Isotherm Models. These approaches were pioneered by Fowler and Guggenheim and Hill and this approach has been applied to modeling of adsorption in microporous adsorbents.

Semiempirical Isotherm Models. Some of these models have been shown to have some thermodynamic inconsistencies and should be used with due care. They include models based on the Polanyi adsorption potential (Dubinin-Radushkevich, Dubinin-Astakhov, Radke-Prausnitz, Toth, UNILAN, and BET).

Isotherm Models for Adsorption of Mixtures. Of the following models, all but the ideal adsorbed solution theory (IAST) and the related heterogeneous ideal adsorbed solution theory (HIAST) have been shown to contain some thermodynamic inconsistencies. They include Markham and Benton, the Leavitt loading ratio correlation (LRC) method, the ideal adsorbed solution (IAS) model, the heterogeneous ideal adsorbed solution theory (HIAST), and the vacancy solution model (VSM).

Adsorption Dynamics. An outline of approaches that have been taken to model mass-transfer rates in adsorbents has been given. Extensive literature exists on the interrelated topics of modeling of mass-transfer rate processes in fixed-bed adsorbers, bed concentration profiles, and breakthrough curves and the related simple design concepts of WES, WUB, and LUB for constant-pattern adsorption.

Reactions on Adsorbents. To permit the recovery of pure products and to extend the adsorbent's useful life, adsorbents should generally be inert and not react with or catalyze reactions of adsorbate molecules. These considerations often affect adsorbent selection or require limits be placed upon the severity of operating conditions to minimize reactions of the adsorbate molecules or damage to the adsorbents.

Adsorbent Principles

Principal Adsorbent Types. Commercially useful adsorbents can be classified by the nature of their structure (amorphous or crystalline), by the sizes of their pores (micropores, mesopores, and macropores), by the nature of their surfaces (polar, nonpolar, or intermediate), or by their chemical composition. All of these characteristics are important in the selection of the best adsorbent for any particular application. However, the size of the pores is the most important initial consideration because if a molecule is to be adsorbed, it must not be larger than the pores of the adsorbent.

Adsorption Properties. Not only do the more highly polar molecular sieve zeolites adsorb more water at lower pressures than do the moderately polar silica gels and alumina gels, but they also hold onto the water more strongly at higher temperatures. For the same reason, temperatures required for thermal regeneration of water-loaded zeolites are higher than for less highly polar adsorbents.

Physical Properties. Physical properties of importance include particle size, density, volume fraction of intraparticle and extraparticle voids when packed into adsorbent beds, strength, attrition resistance, and dustiness. These properties can be varied intentionally to tailor adsorbents to specific applications. See also **Adsorption: Liquid Separation**; and **Molecular Sieves**.

Deactivation. Gradual adsorbent degradation by chemical attack or physical damage commonly occurs in many uses, accompanied by declining separation performance. Allowance for this must be taken into account in design of the process and in scheduling the replacement of spent adsorbents.

Adsorption Processes

Adsorption processes are often identified by their method of regeneration. Temperature-swing adsorption (TSA) and pressure-swing (PSA) are the most frequently applied process cycles for gas separation. Purge-swing cycles and nonregenerative approaches are also applied to the separation of gases. Special applications exist in the nuclear industry. Others take advantage of reactive sorption. Most adsorption processes use fixed beds, but some use moving or fluidized beds.

Design Methods

Design techniques for gas-phase adsorption range from empirical to theoretical. Methods have been developed for equilibrium, for mass transfer, and for combined dynamic performance. Approaches are available for the regeneration methods of heating, purging, steaming, and pressure swing. Several broad reviews have been published on analytical equations describing adsorption, on experimental adsorption processes, and on adsorption design considerations.

Future Directions

Advances in fundamental knowledge of adsorption equilibrium and mass transfer will enable further optimization of the performance of existing adsorbent types. Continuing discoveries of new molecular sieve materials will also provide adsorbents with new combinations of useful properties. New adsorbents and adsorption process will be developed to provide needed improvements in pollution control, energy conservation, and the separation of high value chemicals. New process cycles and new hybrid processes linking adsorption with other unit operations will continue to be developed.

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ADSORPTION: LIQUID SEPARATION. Liquid-phase adsorption has long been used for the removal of contaminants present at low concentrations in process streams. In most cases, the objective is to remove a specific feed component; alternatively, the contaminants are not well defined, and the objective is the improvement of feed quality defined by color, taste, odor, and storage stability.

In contrast to trace impurity removal, the use of adsorption for bulk separation in the liquid phase on a commercial scale is a relatively recent development. This article is devoted mainly to the theory and operation of these liquid-phase bulk adsorptive separation processes.

Adsorbate–Adsorbent Interactions

An adsorbent can be visualized as a porous solid having certain characteristics. When the solid is immersed in a liquid mixture, the pores fill with liquid, which at equilibrium differs in composition from that of the liquid surrounding the particles. These compositions can then be related to each other by enrichment factors that are analogous to relative volatility in distillation. The adsorbent is selective for the component that is more concentrated in the pores than in the surrounding liquid.

A significant advantage of adsorbents over other separative agents lies in the fact that favorable equilibrium-phase relations can be developed for particular separations; adsorbents can be produced that are much more selective in their affinity for various substances than are any known solvents. This selectivity is particularly true of the synthetic crystalline zeolites containing exchangeable cations.

An example of unique selectivity is provided by the use of 5A molecular sieves for the separation of linear hydrocarbons from branched and cyclic types. In this system only the linear molecules can enter the pores; others are completely excluded because of their larger cross section. Thus the selectivity for linear molecules with respect to other types is infinite. In the more usual case, all the feed components access the selective pores, but some components of the mixture are adsorbed more strongly than others. A selectivity between the different components that can be used to accomplish separation is thus established.

Practical Adsorbents

The search for a suitable adsorbent is generally the first step in the development of an adsorption process. A practical adsorbent has four primary requirements: selectivity, capacity, mass transfer rate, and long-term stability. The requirement for adequate adsorptive capacity restricts the choice of adsorbents to microporous solids with pore diameters ranging from a few tenths to a few tens of nanometers.

Traditional adsorbents such as silica, SiO_2; activated alumina, Al_2O_3; and activated carbon, C, exhibit large surface areas and micropore volumes.

TABLE 1. MOLECULAR SIEVE PORE STRUCTURES

Common name	Ring size, number of atoms	Free aperture, nm	Pore structure	Formula
faujasite	12	0.74	3-D	$(Ca, Mg, Na_2, K_2)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}]\cdot 235H_2O$
mordenite	8	0.29×0.57	1-D	$Na_8[(AlO_2)_8(SiO_2)_{40}]\cdot 24H_2O$
	12	0.67×0.7	1-D	
L	12	0.71	1-D	$K_9[(AlO_2)_9(SiO_2)_{27}]\cdot 22H_2O$
ZSM-5	10	0.54×0.56	1-D	$(Na, TPA^a)_3\ [(AlO_2)_3(SiO_2)_{93}\cdot 16H_2O]$
	10	0.51×0.56	1-D	
Erionite	8	0.36×0.52	2-D	$(Ca, Mg, Na_2, K_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}]\cdot 27H_2O$
A	8	0.42	3-D	$Na_{12}\ [(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$

[a] TPA = tetrapropylammonium.

The surface chemical properties of these adsorbents make them potentially useful for separations by molecular class. However, the micropore size distribution is fairly broad for these materials. This characteristic makes them unsuitable for use in separations in which steric hindrance can potentially be exploited.

In contrast to these adsorbents, zeolites offer increased possibilities for exploiting molecular-level differences among adsorbates. Zeolites are crystalline aluminosilicates containing an assemblage of SiO_4 and AlO_4 tetrahedra joined together by oxygen atoms to form a microporous solid, which has a precise pore structure. Nearly 40 distinct framework structures have been identified to date. Table 1 and Figure 1 summarizes some of those structures that have been widely used in the chemical industry. The versatility of zeolites lies in the fact that widely different adsorptive properties may be realized by the appropriate control of the framework structure, the silica-to-alumina ratio (Si/Al), and the cation form.

Commercial Processes

Industrial-scale adsorption processes can be classified as batch or continuous. In a batch process, the adsorbent bed is saturated and regenerated in a cyclic operation. In a continuous process, a countercurrent staged contact between the adsorbent and the feed and desorbent is established by either a true or a simulated recirculation of the adsorbent. The efficiency of an adsorption process is significantly higher in a continuous mode of operation than in a cyclic batch mode. For difficult separations, batch operation may require 25 times more adsorbent inventory and twice the desorbent circulation rate than does a continuous operation. In addition, in a batch mode, the four functions of adsorption, purification, desorption, and displacement of the desorbent from the adsorbent are inflexibly linked, whereas a continuous mode allows more degrees of freedom with respect to these functions, and thus a better overall operation.

Continuous Countercurrent Processes

The need for a continuous countercurrent process arises because the selectivity of available adsorbents in a number of commercially important separations is not high. In the *p*-xylene system, for instance, if the liquid around the adsorbent particles contains 1% *p*-xylene, the liquid in the pores contains about 2% *p*-xylene at equilibrium. Therefore, one stage of contacting cannot provide a good separation, and multistage contacting must be provided in the same way that multiple trays are required in fractionating materials with relatively low volatilities.

Since the 1960s the commercial development of continuous countercurrent processes has been almost entirely accomplished by using a flow scheme that simulates the continuous countercurrent flow of adsorbent and process liquid without the actual movement of the adsorbent. The idea of a simulated moving bed (SMB) can be traced back to the Shanks system for leaching soda ash.

Such a concept was originally used in a process developed and licensed by UOP under the name UOP Sorbex. The extent of commercial of Sorbex processes is shown in Table 2. Other versions of the SMB system are also used commercially. Toray Industries built the Aromax process for the production of *p*-xylene. Illinois Water Treatment and Mitsubishi have commercialized SMB processes for the separation of fructose from dextrose.

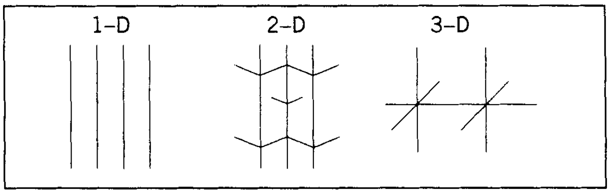

Fig. 1. Schematic diagram of molecular sieve pore structure. See Table 1

Cyclic-Batch Processes

Continuous processes have wide application in different areas of the chemical industry. The separation efficiency of a continuous process is generally higher than that of a batch or cyclic-batch process. However, in some applications the cyclic-batch process may be preferred because of the complexity of design and the difficulty of controlling the continuous processes. Examples of commercial cyclic-batch adsorption processes operating in liquid phase include the UOP methanol recovery (UOP MRU) and oxygenate removal (UOP ORU) processes, which separate oxygenates from C_4 hydrocarbons; the UOP Cyclesorb process, which separates fructose from glucose; and ion-exclusion processes for recovering sucrose from molasses.

Liquid Chromatography

Conventional liquid chromatography has not attained great commercial significance in the area of large-scale bulk separations from the liquid phase. In analytical chromatography, the primary objective is to maximize the resolution between two components subject to some restrictions on the maximum time of elution. As a result, the feed pulse loading is minimized, and the number of theoretical plates is maximized. In preparative chromatography, the objective is to maximize production rate as well as reduce capital and operating costs at a given separation efficiency. The adsorption column is therefore commonly run under overload conditions with a finite feed pulse width. The choice of operating conditions for preparative chromatography has been discussed. In production chromatography, the optimal pulse sequence occurs when the successive pulses of feed are introduced at intervals such that the feed components are just resolved both within a given sample and between adjacent samples.

Outlook

Liquid adsorption processes hold a prominent position in several applications for the production of high purity chemicals on a commodity scale. Many of these processes were attractive when they were first introduced to the industry and continue to increase in value as improvements in adsorbents, desorbents, and process designs are made. The UOP Parex process alone has seen four generations of adsorbent and four generations of desorbent.

The value of many chemical products from pesticides to pharmaceuticals to high performance polymers, is based on unique properties of a particular isomer from which the product is ultimately derived. Often the purity requirement for the desired product includes an upper limit on the content of

TABLE 2. UOP SORBEX PROCESSES FOR COMMODITY CHEMICALS

UOP processes	Separation	Licensed units
Parex	*p*-xylene from C_8 aromatics	53
Molex	*n*-paraffins from branched and cyclic hydrocarbons	33
Olex	olefins from paraffins	6
Cymex	*p*- or *m*-cymene from cymene isomers	1
Cresex	*p*- or *m*-cresol from cresol isomers	1
Sarex	fructose from dextrose plus polysaccharides	5
Total		*99*

one or more of the other isomers. This separation problem is a complicated one, but one in which adsorptive separation processes offer the greatest chances for success.

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AERATION. A process of contacting a liquid with air, often for the purpose of releasing other dissolved gases, or for increasing the quantity of oxygen dissolved in the liquid. Aeration is commonly used to remove obnoxious odors or disagreeable tastes from raw water. The principle of aeration is also used in the treatment of sewage by a method known as the activated sludge process. The sewage is allowed to flow into an aeration tank where it is mixed with a predetermined volume of sludge. Compressed air is introduced which agitates the mixture and furnishes oxygen that is necessary for certain biological changes. Sewage may also be aerated by mechanically actuated paddles that rotate the liquid and constantly bring a fresh surface in contact with the atmosphere.

Aeration is of importance in the fermentation industries. In the manufacture of baker's yeast, penicillin, and other antibiotics, an adequate air supply is required for optimum yields in certain submerged fermentation processes.

Aeration can be accomplished by allowing the liquid to fall in a thin film or to be sprayed in the form of droplets in air at atmospheric pressure; or the air, under pressure, may be bubbled into the liquid by means of a sparger, or other device that creates thousands of small bubbles, thus providing maximum contact area between the air and the liquid.

AEROGELS. Aerogels are solid materials that are so porous that they contain mostly air. Almost all applications of aerogels are based on the unique properties associated with a highly porous network. Envision an aerogel as a sponge consisting of many interconnecting particles which are so small and so loosely connected that the void space in the sponge, the pores, can make up over 90% of its volume. The ability to prepare materials of such low density, and perhaps more importantly, to vary the density in a controlled manner, is indeed what make aerogels attractive in many applications.

Sol–Gel Chemistry

Inorganic Materials. Sol–gel chemistry involves first the formation of a sol, which is a suspension of solid particles in a liquid, then of a gel, which is a diphasic material with a solid encapsulating a solvent. A detailed description of the fundamental chemistry is available in the literature. The chemistry involving the most commonly used precursors, the alkoxides ($M(OR)_m$), can be described in terms of two classes of reactions:

$$\text{Hydrolysis} \quad -\mathrm{M{-}OR} + \mathrm{H_2O} \longrightarrow -\mathrm{M{-}OH} + \mathrm{ROH}$$

$$\text{Condensation} \quad -\mathrm{M{-}OH} + \mathrm{XO{-}M}- \longrightarrow -\mathrm{M{-}O{-}M} + \mathrm{XOH}$$

where X can either be H or R, an alkyl group

The important feature is that a three-dimensional gel network comes from the condensation of partially hydrolyzed species. Thus, the microstructure of a gel is governed by the rate of particle (cluster) growth and their extent of crosslinking or, more specifically, by the *relative* rates of hydrolysis and condensation.

Acid- and base-catalyzed gels yield micro- (pore width less than 2 nm) and meso-porous (2–50 nm) materials, respectively, upon heating. An acid-catalyzed gel which is weakly branched and contains surface functionalities that promote further condensation collapses to give micropores. This example highlights a crucial point: *the initial microstructure and surface functionality of a gel dictates the properties of the heat-treated product.*

Besides pH, other preparative variables that can affect the microstructure of a gel, and consequently, the properties of the dried and heat-treated product include water content, solvent, precursor type and concentration, and temperature.

In the preparation of a two-component system, the minor component can either be a network modifier or a network former. In the latter case, the distribution of the two components, or mixing, at a molecular level is governed by the *relative* precursor reactivity. Qualitatively good mixing is achieved when two precursors have similar reactivities. When two precursors have dissimilar reactivities, the sol–gel technique offers several strategies to prepare well-mixed two-component gels. Two such strategies are prehydrolysis, which involves prereacting a less reactive precursor and chemical modification, which involves slowing down a more reactive precursor. The ability to control microstructure *and* component mixing is what sets sol–gel apart from other methods in preparing multicomponent solids.

Organic Materials. The sol–gel chemistry of organic materials is similar to that of inorganic materials. The first organic aerogel was prepared by the aqueous polycondensation of resorcinol with formaldehyde using sodium carbonate as a base catalyst.

Resorcinol–formaldehyde gels are dark red in color and do not transmit light. The preparation of melamine–formaldehyde gels, which are colorless and transparent, is also aqueous-based. Since water is deleterious to a gel's structure at high temperatures and immiscible with carbon dioxide (a commonly used supercritical drying-agent), these gels cannot be supercritically dried without a tedious solvent-exchange step. In order to circumvent this problem, an alternative synthetic route of organic gels that is based upon a phenolic–furfural reaction using an acid catalyst has been developed. The solvent-exchange step is eliminated by using alcohol as a solvent. The phenolic–furfural gels are dark brown in color.

Carbon aerogels can be prepared from the organic gels mentioned above by supercritical drying with carbon dioxide and a subsequent heat-treating step in an inert atmosphere.

Despite these changes, the carbon aerogels are similar in morphology to their organic precursors, underscoring again the importance of structural control in the gelation step. Furthermore, changing the sol–gel conditions can lead to aerogels that have a wide range of physical properties.

Inorganic–Organic Hybrids. One of the fastest growing areas in sol–gel processing is the preparation of materials containing both inorganic and organic components, because many applications demand special properties that only a combination of inorganic and organic materials can provide. In this regard, sol–gel chemistry offers a real advantage because its mild preparation conditions do not degrade organic polymers, as would the high temperatures that are associated with conventional ceramic processing techniques. The voluminous literature on the sol–gel preparation of inorganic–organic hybrids can be found in several recent reviews and the references therein.

Preparation and Manufacturing

Supercritical Drying. The development of aerogel technology from the original work of Kistler to about late 1980s has been reviewed. Over this period, supercritical drying was the dominant method in preparing aerogels. Several advances, summarized in Table 1, have made possible the relatively safe supercritical drying of aerogels in a matter of hours. In recent years, the challenge has been to produce aerogel-like materials without using supercritical drying at all in an attempt to deliver economically competitive products.

Supercritical drying should be considered as part of the aging process, during which events such as condensation, dissolution, and reprecipitation

TABLE 1. IMPORTANT DEVELOPMENTS IN THE PREPARATION OF AEROGELS

Decade	Developments
1930	Using inorganic salts as precursors, alcohol as the supercritical drying agent, and a batch process; a solvent-exchange step was necessary to remove water from the gel.
1960	Using alkoxides as precursors, alcohol as the supercritical drying agent, and a batch process; the solvent exchange step was eliminated.
1980	Using alkoxides as precursors, carbon dioxide as the drying agent, and a semicontinuous process; the drying procedure became safer and faster. Introduction of organic aerogels.
1990	Producing aerogel-like materials without supercritical drying at all; preparation of inorganic–organic hybrid materials.

can occur. The extent to which a gel undergoes aging during supercritical drying depends on the structure of the initial gel network. A higher drying temperature changes the particle structure of base-catalyzed silica aerogels but not that of acid-catalyzed ones. Gels that have uniform-sized pores can withstand the capillary forces during drying better because of a more uniform stress distribution. Such gels can be prepared by a careful manipulation of sol–gel parameters such as pH and solvent or by the use of so-called drying control chemical additives (DCCA).

Carbon dioxide is the drying agent of choice if the goal is to stabilize kinetically constrained structure, and materials prepared by this low-temperature route are referred to by some people as *carbogels*. In general, carbogels are also different from aerogels in surface functionality, in particular hydrophilicity.

However, even with carbon dioxide as a drying agent, the supercritical drying conditions can affect the properties of a product. Other important drying variables include the path to the critical point, composition of the drying medium, and depressurization.

For some applications it is desirable to prepare aerogels as thin films that are either self-supporting or supported on another substrate. All common coating methods such as dip coating, spin coating, and spray coating can be used to prepare gel films.

In all the processes discussed above, the gelation and supercritical drying steps are done sequentially. Recently a process that involves the direct injection of the precursor into a strong mold body followed by rapid heating for gelation and supercritical drying to take place was reported. By eliminating the need of forming a gel first, this entire process can be done in less than three hours per cycle. Besides saving time, gel containment minimizes some stresses and makes it possible to produce near net-shape aerogels and precision surfaces. The optical and thermal properties of silica aerogels thus prepared are comparable to those prepared with conventional methods.

Ambient Preparations. Economic and safety considerations have provided a strong motivation for the development of techniques that can produce aerogel-like materials at ambient conditions, i.e., without supercritical drying. The strategy is to minimize the deleterious effect of capillary pressure which is given by:

$$P = 2\sigma\cos(\theta)/r$$

where P is capillary pressure, σ is surface tension, θ is the contact angle between liquid and solid, and r is pore radius.

The equation above suggests that one approach would be to use a pore liquid that has a low surface tension. In fact, with a pore liquid that has a sufficiently small surface tension, ambient pressure acid catalyzed aerogels with comparable pore volume and with bulk density to those prepared with supercritical drying (see Fig. 1) have been produced.

For base-catalyzed silica gels, it has been shown that modifying the surface functionality is an effective way to minimize drying shrinkage. In particular, surface hydroxyl groups, the condensation of which leads to pore collapse, can be "capped off" via reactions with organic groups such as tetraethoxysilane and trimethylchlorosilane. This surface modification approach (also referred to as surface derivatization), initially developed for bulk specimens, has recently been applied to the preparation of thin films.

In changing surface hydroxyls into organosilicon groups, surface modification has an additional advantage of producing hydrophobic gels. This feature, namely the immiscibility of surface-modified gel with water, has led to the development of a rapid extractive drying process shown in Figure 2. This ambient pressure process offers improved heat transfer rates and, in turn, greater energy efficiency without compromising desirable aerogel properties.

Another approach to produce aerogels without supercritical drying is freeze drying, in which the liquid–vapor interface is eliminated by freezing a wet gel into a solid and then subliming the solvent to form what is known as a *cryogel*. The limited data available on freeze drying suggest that it might not be as attractive as the above ambient approaches in producing aerogels on a commercial scale.

Properties

Table 2 summarizes the key physical properties of silica aerogels. A range of values is given for each property because the exact value is dependent on the preparative conditions and, in particular, on density.

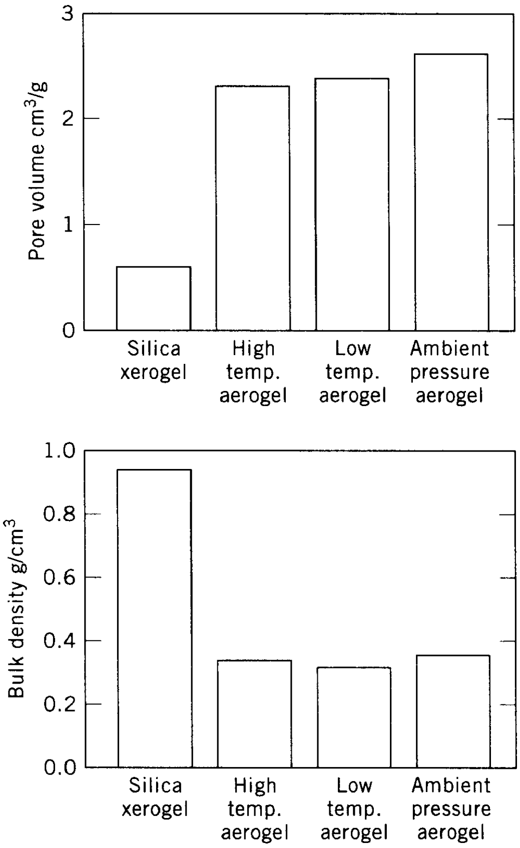

Fig. 1. Comparison of physical properties of silica xerogels and aerogels. Note the similar properties of the aerogels prepared with and without supercritical drying. Reproduced from C. J. Brinker and co-workers, *Mat. Res. Soc. Symp. Proc.* **271**, 567 (1992). Courtesy of the Materials Research Society

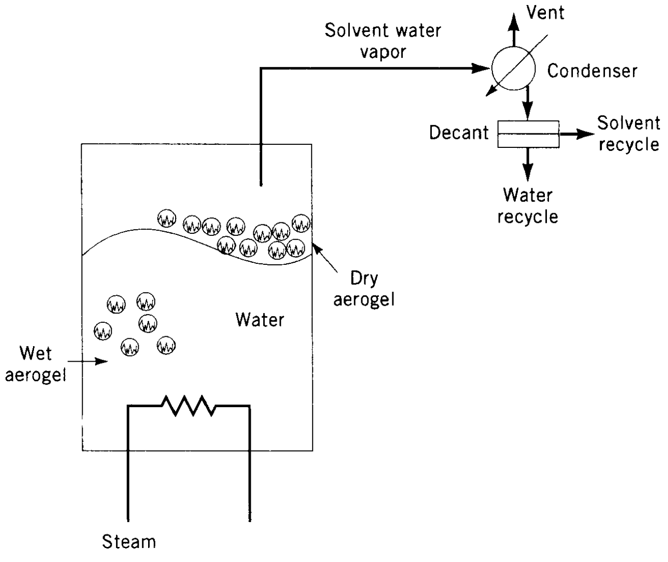

Fig. 2. Schematic diagram of an extractive drying process that produces aerogels at ambient pressure. Reproduced from D. M. Smith and co-workers, *Mat. Res. Soc. Symp. Proc.* **431**, 291 (1996). Courtesy of the Materials Research Society

Applications

Aerogels are used in thermal insulation, catalysis, detection of high energy particles, piezoceramic, ultrasound transducers, integrated circuits, and as dehydrating agents.

Summary

It has been hailed as the world's lightest solid, and a near-magic material. Yet more than 70 years after chemists first discovered the extraordinary form of matter called "aerogels," it's been used almost exclusively by space researchers and in niche markets.

TABLE 2. TYPICAL VALUES OF PHYSICAL PROPERTIES OF SILICA AEROGELS

Property	Values
density, kg/m^3	3–500
surface area, m^2/g	800–1000
pore sizes, nm	1–100
pore volume, cm^3/g	3–9
porosity, %	75–99.9
thermal conductivity, W/(m·K)	0.01–0.02
longitudinal sound velocity, m/s	100–300
acoustic impedance, kg/(m^2·s)	10^3–10^6
dielectric constant	1–2
Young's modulus, N/m^2	10^6–10^7

Now, Boston-based Cabot Corp. is rolling out the first major commercial application of the silicon-based material: window and skylight panels that use aerogels for heat and sound insulation while allowing light to pass through.

While large commercial markets have been long in coming, aerogels have been used in NASA projects, such as Mars exploration vehicles and a space probe capturing comet-tail dust.

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AEROSOLS. A colloidal system in which a gas, frequently air, is the continuous medium, and particles of solids or liquid are dispersed in it. Aerosol thus is a common term used in connection with air pollution control. Studies of the particle size distribution of atmospheric aerosols have shown a multimodal character, usually with a bimodal mass, volume, or surface area distribution and frequently trimodal surface area distribution near sources of fresh combustion aerosols. The coarse mode (2 micrometers and greater) is formed by relatively large particles generated mechanically or by evaporation of liquid from droplets containing dissolved substances. The nuclei mode (0.03 micrometer and smaller) is formed by condensation of vapors from high-temperature processes, or by gaseous reaction products. The intermediate or accumulation mode (from 0.1 to 1.0 micrometer) is formed by coagulation of nuclei. Study of the behavior of the particles in each mode has led to the belief that the particles tend to form a stable aerosol having a size distribution ranging from about 0.1 to 1.0 micrometer. The larger particles (in excess of 1.0 micrometer in size) settle, or fall out, whereas the very fine particles (smaller than 0.1 micrometer) tend to agglomerate to form larger particles which remain suspended. The nuclei mode tends to be highly transient and is concentration limited by coagulation with both other nuclei and also particles in the accumulation mode. It further appears that additional growth of particle size from the accumulation mode to the coarse mode is limited to 5% or less (by mass). Thus, the particulate content of a source emission and the ambient air can be viewed as composed of two portions, i.e., settle-able and suspended.

Both settle-able and suspended atmospheric particles have deleterious effects upon the environment. The settle-able particles can affect health if assimilated and also can cause adverse effects on materials, crops, and vegetation. Further, such particles settle out in streams and upon land where soluble substances, sometimes including hazardous materials, are dissolved out of the particles and thus become pollutants of soils and surface and ground waters. Suspended atmospheric particulate matter has undesirable effects on visibility and, if continuous and of sufficient concentration, possible modifying effects on the climate. Importantly, it is particles within a size range from 2 to 5 micrometers and smaller that are considered most harmful to health because particles of this size tend to penetrate the body's defense mechanisms and reach most deeply into the lungs.

The term aerosol is also applied to a form of packaging in which a gas under pressure, or a liquefied gas that has a pressure greater than atmospheric pressure at ordinary temperatures, is used to spray a liquid. The result of the spraying process is to produce a mist of small liquid droplets in air, although not necessarily a stable colloidal system. Numerous products, such as paints, clear plastic solutions, fire-extinguishing compounds, insecticides, and waxes and cleaners, are packaged in this fashion for convenience. Food products, such as topping and whipped cream, also are packaged in aerosol cans.

For a number of years, chlorofluorocarbons were the most popular source of pressure for these cans. Because of concern in recent years over the reactions of chlorofluorocarbons in the upper atmosphere of the earth that appear to be leading to a deterioration of the ozone layer, some countries have banned their use in aerosol cans. Manufacturers have turned to other gases or to conveniently operated hand pumps. See also **Colloid Systems**; and **Pollution (Air)**.

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AFFINITY. The tendency of an atom or compound to react or combine with atoms or compounds of different chemical constitution. For example, paraffin hydrocarbons were so named because they are quite unreactive, the word *paraffin* meaning "very little affinity." The hemoglobin molecule has a much greater affinity for carbon monoxide than for oxygen. The free energy decrease is a quantitative measure of chemical affinity.

AGAR. Sometimes called *agar-agar,* this is a gelatine-like substance which is prepared from various species of red algae growing in Asiatic waters. The prepared product appears in the form of cakes, coarse granules, long shreds, or in thin sheets. It is used extensively alone or in combination with various nutritive substances, as a medium for culturing bacteria and various fungi. See also **Gums and Mucilages**.

AGATE. Agate is a variety of chalcedony, whose variegated colors are distributed in regular bands or zones, in clouds or in dendritic forms, as in moss agate.

The banding is often very delicate with parallel lines of different colors, sometimes straight, sometimes undulating or concentric. The parallel bands represent the edges of successive layers of deposition from solution in cavities in rocks that generally conform to the shape of the enclosing cavity.

As agate is an impure variety of quartz it has the same physical properties as that mineral. It is named from the river Achates in Sicily where it has been known from the time of Theophrastus.

Agate is found in many localities; India, Brazil, Uruguay, and Germany are notable for fine specimens.

Onyx is a variety of agate in which the parallel bands are perfectly straight and can be used for the cutting of cameos. Sardonyx has layers of dark reddish-brown carnelian alternating with light and dark colored layers of onyx.

See also **Chalcedony**; and **Quartz**.

AGENT ORANGE. Common name for a 50–50% mixture of the herbicides 2,4,5-T and 2,4-D, once widely used by the military as a defoliant. The mixture contains dioxin as a contaminant. See also **Dioxin**; and **Herbicides**.

AGGLOMERATION. This term connotes a gathering together of smaller pieces or particles into larger size units. This is a very important operation in the process industries and takes a number of forms. Specific advantages of agglomeration include: increasing the bulk density of a material; reducing storage-space needs; improving the handling qualities of bulk materials; improving heat-transfer properties; improving control over solubility; reducing material loss and lessening of pollution, particularly of dust; converting waste materials into a more useful form and reducing labor costs because of resulting improved handling efficiency.

The principal means used for agglomerating materials include (1) compaction, (2) extrusion, (3) agitation, and (4) fusion.

Tableting is an excellent example of compaction. In this operation, loose material, such as a powder, is compressed between two opposing surfaces, or compacted in a die or cavity. Some tableting machines use the action of two opposing plungers that operate within a cavity. Resulting tablets may range from $\frac{1}{8}$ to 4 inches (3 millimeters to 10 centimeters) in diameter. Uniformity and dimensional precision are outstanding. Numerous pharmaceutical products are formed in this manner, as well as some metallic powders and industrial catalysts.

Pellet mills exemplify the use of extrusion. In some designs the charge material is forced out of cylindrical or other shaped holes located on the periphery of a cylinder within which rollers and spreaders force the bulk materials through the openings. A knife cuts the extruded pellets to length as they are forced through the dies.

The *rolling drum* is the simplest form of aggregation using agitation. Aggregates are formed by the collision and adherence of the bulk particles in the presence of a liquid binder or wetting agent to produce what essentially is a "snowball" effect. As the operation continues, the spheroids become larger. The strength and hardness of the enlarged particles are determined by the binder and wetting agent used. The operation is followed by screening, with recycling of the fines.

The *sintering process* utilizes fusion as a means of size-enlargement. This process, used mainly for ores and minerals and some powdered metals, employs heated air that is passed through a loose bed of finely ground material. The particles partially fuse together without the assistance of a binder. Sintering frequently is accompanied by the volatilization of impurities and the removal of undesired moisture.

The *spray-type* agglomerator utilizes several principles. Loosely bound clusters or aggregates are formed by the collision and coherence of the fine particles and a liquid binder in a turbulent stream. The mixing vessel consists of a vertical tank, around whose lower periphery are mounted spray nozzles for introduction of the liquid. A suction fan draws air through the bottom of the tank and creates an updraft within the mixing vessel. Materials spiral downward through the mixing chamber, where they meet the updraft and are held in suspension near the portion of the vessel where the liquids are injected. The liquids are introduced in a fine mist. Individual droplets gather the solid particles until the resulting agglomerate overcomes the force of the updraft and falls to the bottom of the vessel as finished product.

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AGGLUTINATION. The combination or aggregation of particles of matter under the influence of a specific protein. The term is usually restricted to antigen-antibody reactions characterized by the clumping together of visible cells such as bacteria orerythrocytes.

See also **Aggregation**.

AGGLUTININ. One of a class of substances found in blood to which certain foreign substances or organisms have been added or admixed. As the name indicates, agglutinins have the characteristic property of causing agglutination, especially of the foreign substances or organisms responsible for their formation.

See also **Agglutination**.

AGGREGATE. The solid conglomerate of inert particles which are cemented together to form concrete are called aggregate. A well-graded mixture of fine and coarse aggregates is used to obtain a workable, dense mix. The aggregate may be classed as fine or coarse depending upon the size of the individual particles. The specifications for the concrete on any project will give the limiting sizes that will distinguish between the two classifications. Fine aggregate generally consists of sand or stone screenings while crushed stone, gravel, slag or cinders are used for the coarse aggregate. The aggregates should be strong, clean, durable, chemically inert, free of organic matter, and reasonably free from flat and elongated particles since the strength of the concrete is dependent upon the quality of the aggregates as well as the matrix of cementing material. See also **Concrete**.

AGGREGATION. This overall operation may be considered to include the more specific designations of *agglutination, coagulation*, and *flocculation*. These terms imply some change in the state of dispersion of sols or of macromolecules in solution.

Agglutination generally refers to the aggregation of particulate matter mediated by an interaction with a specific protein. More specifically, the term refers to antigen-antibody reactions characterized by a clumping together of visible cells, such as bacteria or erythrocytes. The distinguishing feature of these reactions appears to be the presence of special areas where the orientation of active groups permits specific interaction of antigen with antibody. There is evidence that the forces involved may include hydrogen bonding, electrostatic attraction, and London-van der Waals forces. The clumping of the fat globules in milk has been described as an agglutination by the proteins of the euglobulin fraction. When the fat globules are dispersed in a dilute salt solution, the addition of this protein fraction induces normal creaming. Although this action is nonspecific, the same protein fraction causes agglutination of certain bacteria when they are added to milk.

Coagulation of a hydrophobic sol may be brought about by the addition of small amounts of electrolytes. Coagulation may be rapid, occurring in seconds, or slow, requiring months for completion. The resultant coagula contain relatively small proportions of the dispersion medium, in contrast with jellies formed from hydrophilic systems. Sometimes it is found that what at first appeared to be a homogeneous liquid becomes turbid and distinctly nonhomogeneous. Systems which are intermediate between true hydrophobic sols and hydrophilic sols are encountered frequently, so that in common usage the word *coagulation* is applied to such diverse phenomena as the clotting of blood by thrombin or the clotting of milk by rennin.

Flocculation is generally considered synonymous with coagulation, but is widely used in connection with certain kinds of applications. If one considers only hydrophilic systems, it is apparent that an important factor in flocculation is the solvation of the particles, despite the common presence of an electric charge. Since stability appears to depend upon solute-solvent interactions and solubility properties, flocculation can frequently be brought about by either of two pathways. The addition of salts may compress the double layer, leaving the macromolecules stabilized by a diffuse solvation shell. The addition of alcohol or acetone will dehydrate the particles, leading to instability and flocculation. Alternatively, the alcohol or acetone may be added first, which will convert the particle to one of hydrophobic character stabilized largely by the electric double layer. Such a sol can be coagulated by the addition of small amounts of electrolytes.

See also **Colloid Systems**

AIChE. The American Institute of Chemical Engineers was founded in Philadelphia, Pennsylvania, in 1908 to serve what, at that time, was an emerging new engineering discipline, *chemical engineering*. The general aim of the Institute is to promote excellence in the development and practice of chemical engineering through semiannual district meeting and an annual national meeting for the presentation and discussion of technical papers and the exhibition of equipment and materials used in chemical engineering projects. The Institute publishes several periodicals, including the *AIChE Journal, International Chemical Engineering*, and *Chemical Engineering Progress*. Technical divisions of the AIChE include Computer and Systems Technology, Engineering and Construction Contracting, Environmental Technology, Food, Pharmaceutical and Bioengineering, Forest Products, Fuels and Petrochemicals, Heat Transfer and Energy Conversion, Management, Materials Engineering and Sciences, Nuclear Engineering, Safety and Health, and Separations Technology. The Institute sponsors research projects in cooperation with corporate, governmental, and institutional sources, including the Center for Chemical Process Safety (CCPS), the Center for Waste Reduction Technologies (CWRT), the Design Institute for Emergency Relief Systems (DIERS), the Design Institute for Physical Property Data (DIPRR), the Process Data Exchange Institute (PDXI), and the Research Institute for Food Engineering. Headquarters of the AIChE is in New York City.

AIR. In addition to being the principal substance of the earth's atmosphere, air is a major industrial medium and chemical raw material. The average composition of dry air at sea level, disregarding unusual concentrations of certain pollutants, is given in Table 1. The amount of water vapor in the air varies seasonally and geographically and is a factor of large importance where air in stoichiometric quantities is required for reaction processes, or where water vapor must be removed in air-conditioning and compressed-air systems. The water content of air for varying conditions of temperature and pressure is shown in Table 2. The

TABLE 1. COMPOSITION OF AIR

Constituent	Percent by weight	Percent by volume
Oxygen (O_2)	23.15	20.95
Ozone (O_3)	1.7×10^{-6}	0.00005
Nitrogen (N_2)	75.54	78.08
Carbon dioxide (CO_2)	0.05	0.03
Argon (Ar)	1.26	0.93
Neon (Ne)	0.0012	0.0018
Krypton (Kr)	0.0003	0.0001
Helium (He)	0.00007	0.0005
Xenon (Xe)	5.6×10^{-5}	0.000008
Hydrogen (H_2)	0.000004	0.00005
Methane (CH_4)	trace	trace
Nitrous oxide (N_2O)	trace	trace

TABLE 2. WATER CONTENT OF SATURATED AIR

Temperature (F)	(C)	Water content (Pounds in 1 Pound of Air, or Kilograms in 1 Kilogram of Air)
40	4.44	0.00520
45	7.22	0.00632
50	10	0.00765
55	12.8	0.00920
60	15.6	0.01105
65	18.3	0.01322
70	21.1	0.01578
75	23.9	0.01877
80	26.7	0.02226
85	29.4	0.02634
90	32.2	0.03108
95	35.0	0.03662
100	37.8	0.04305
105	40.6	0.05052

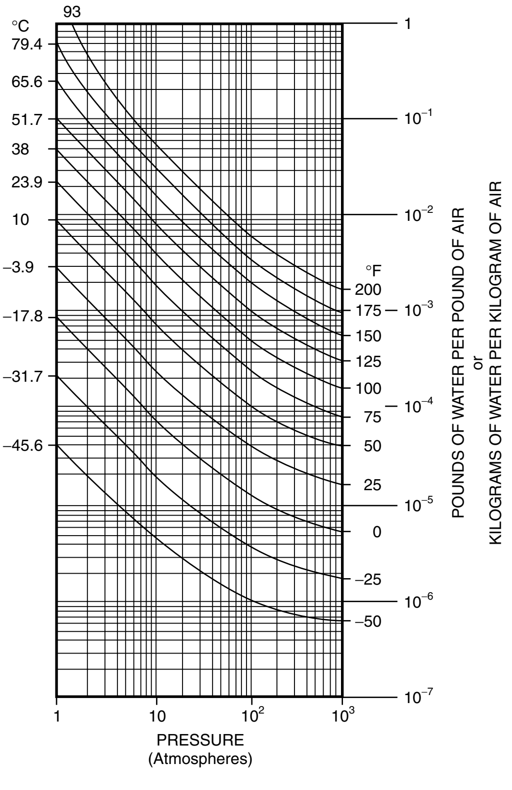


Fig. 1. Water content of saturated air at various temperatures and pressures

water content of saturated air at various temperatures is shown in Fig. 1. See also **Oxygen**; **Nitrogen**; and **Pollution (Air)**.

ALABANDITE. Manganese sulfide, MnS. Associated with pyrite, sphalerite, and galena in metallic sulfide vein deposits.

ALABASTER. A fine-grained variety of the mineral gypsum, formerly much used for vases and statuary. It is usually white in color or may be of other light, pleasing tints.

The word alabaster is derived from the Greek name for this substance. See also **Gypsum**.

ALANINE. See **Amino Acids**.

ALBERTITE. An oxygenated hydrocarbon that differs from asphaltum slightly in that it is not completely soluble in turpentine, nor can it be perfectly fused. Specific gravity, 1.097, pitchy luster, dark brown to black color. Occurs in veins from 1 to 16 feet (0.3 to 5 meters) wide in the Albert Shale of Albert County, New Brunswick.

ALBUMIN. An albumin is a member of a class of proteins which is widely distributed in animal and vegetable tissues. Albumins are soluble in water and in dilute salt solutions, and are coagulable by heat.

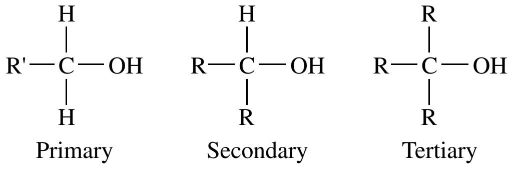
Albumin is of great importance in animal physiology; in man it constitutes about 50% of the plasma proteins (blood) and is responsible to a great extent for the maintenance of osmotic equilibrium in the blood. The high molecular weight (68,000) of the albumin molecule prevents its excretion in the urine; the appearance of albumin may indicate kidney damage.

ALCHEMY. The predecessor of chemistry, practiced from as early as 500 BC through the 16th century. Its two principal goals were transmutation of the baser metals into gold and discovery of a universal remedy. Modern chemistry grew out of alchemy by gradual stages.

ALCOHOL. A term commonly used to designate ethyl alcohol or ethanol. See **Ethyl Alcohol**. Also a class of organic compounds. See **Alcohols**.

ALCOHOLATE. Replacement of the hydrogen in the hydroxyl group of an alcohol by a metal, particularly a metal that forms a strong base, results in formation of an alcoholate. An example is sodium ethylate, C_2 H_5 ONa.

ALCOHOLS. The alcohols may be regarded as hydrocarbon derivatives in which the hydroxyl group (OH) replaces hydrogen on a saturated carbon. Alcohols are classified as *primary, secondary*, or *tertiary*, according to the number of hydrogen atoms that are bonded to the carbon atom with the hydroxyl substituent. Alcohols also may be regarded as alkyl derivatives of water. Thus, alcohols with a small hydrocarbon group tend to be more like water in properties than a hydrocarbon of the same number. Alcohols with a large hydrocarbon group are found to have physical properties similar to a hydrocarbon of the same structure. Some comparisons are given in Table 1. Structures are summarized by:



where $R' = H$, alkyl, aryl; $R =$ alkyl, aryl.

In addition to the basic classification as primary, secondary, or tertiary, alcohols may be further grouped according to other structural features. *Aromatic alcohols* contain an aryl group attached to the carbon having the hydroxyl function; *aliphatic alcohols* contain only aliphatic groups. The prefix *iso* usually indicates branching of the carbon chain.

Alcohols containing two hydroxyl groups are called *dihydric alcohols* or *glycols*. Ethylene glycol, $HOCH_2CH_2OH$, trimethylene glycol, $HOCH_2CH_2CH_2CH_2OH$, and 1,4-butanediol are examples of industrially important glycols. Glycerol, $HOCH_2CHOHCH_2OH$, has three hydroxyl groups per molecule and is a *trihydric* alcohol. Physical properties of alcohols containing more than one hydroxyl group can be estimated by considering the number of carbons for each hydroxyl group as in the case of simple alcohols.

TABLE 1. COMPARISON OF PHYSICAL PROPERTIES OF ALCOHOLS AND HYDROCARBONS

Alcohol	Hydrocarbon	Formula	Properties
Methanol		CH_3OH	Liquid, water soluble, bp. 65°C
	Methane	$CH_3{}^-H$	Gas, water insoluble
Ethanol		CH_3CH_3OH	Liquid, water soluble, bp. 78.5°C
	Ethane	$CH_3CH_2{}^-H$	Gas, water insoluble
Tetradecanol		$CH_3\ (CH_3)_{12}CH_2OH$	Liquid, water insoluble, bp. 263.2°C
	Tetradecane	$CH_3(CH_2)_{12}CH_2{}^-H$	Liquid, water insoluble, bp. 253.5°C

Reactions of Alcohols

Alcohols undergo a large number of reactions. However, these reactions may be grouped into a few general types. Reactions of alcohols may involve the O−H or C−O bonds. Ester formation and salt formation are examples of the former class, while conversion to halides is an example of the latter type.

−O−H Bond Cleavage

$$ROH + CH_3COOH \overset{H_+}{\rightleftharpoons} CH_3COOR + H_2O \qquad (1)$$

$$ROH + K \longrightarrow RO^-K^+ + \tfrac{1}{2}H_2 \qquad (2)$$

C−O Bond Cleavage

$$RCH_2OH + HCl \xrightarrow[170°C]{ZnCL_2} RCH_2Cl + H_2O \qquad (3)$$

Many industrially important substitution reactions of alcohols are conducted in the vapor phase over a catalyst. Only primary alcohols give satisfactory yields of product under these conditions.

$$CH_3OH + H_2S \xrightarrow{K_2WO_4} CH_3SH + H_2O \qquad (4)$$

$$RCH_2OH + (CH_3)_2NH \xrightarrow{Al_2O_3} RCH_2N(CH_3)_2 + H_2O \qquad (5)$$

Production of Alcohols

Lower alcohols (amyl and below) are prepared by (a) hydrogeneration of carbon monoxide (yields methanol), (b) olefin hydration (yields ethanol, isopropanol, secondary and tertiary butanol), (c) hydrolysis of alkyl chlorides, (d) direct oxidation, and (e) the OXO process.

$$C = O + 2\ H_2 \longrightarrow CH_3OH \qquad (6)$$

$$CH_3CH = CH_2 + H_2O \xrightarrow{H^+} CH_3CHOHCH_3 \qquad (7)$$

$$C_5H_{11}Cl + H_2O \longrightarrow \underset{\text{(mixture of isomers)}}{C_5H_{11}OH} \qquad (8)$$

Most higher alcohols (hexanol and higher) and primary alcohols of three carbons or more are synthesized by one of four general processes, or derived from a structurally related natural product. See also **Organic Chemistry**.

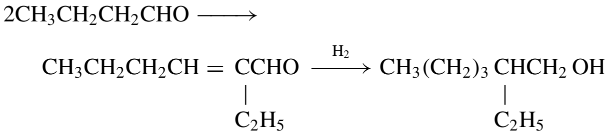
The OXO Process

An olefin may be hydroformylated to a mixture of aldehydes. The aldehydes are readily converted to alcohols by hydrogenation. Many olefins from ethylene to dodecenes are used in the OXO reaction. OXO alcohols are typically a mixture of linear and methyl branched primary alcohols. See also **Oxo Process**.

$$RCH = CH_2 + CO + H_2 \qquad (9)$$
$$\longrightarrow [RCH_2CH_2CHO + RCH(CHO)CH_3]$$

Aldol Condensation

Aldehydes may also be dimerized by an aldol condensation reaction to give a branched unsaturated aldehyde. This may be converted to a branched alcohol by hydrogenation. See also **Aldol Condensation**.

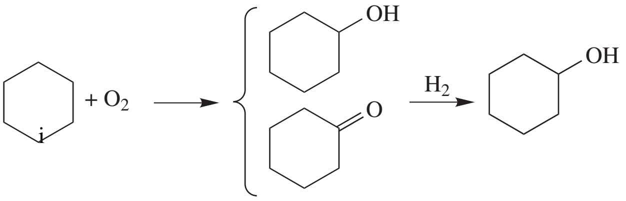


$$2CH_3CH_2CH_2CHO \longrightarrow \qquad (10)$$
$$CH_3CH_2CH_2CH = \underset{\displaystyle C_2H_5}{\underset{|}{C}}CHO \xrightarrow{H_2} CH_3(CH_2)_3\,\underset{\displaystyle C_2H_5}{\underset{|}{C}}HCH_2\,OH$$

Alcohols from an aldol reaction may be linear if acetaldehyde is a reactant, but usually aldol alcohols are branched primary alcohols. An aldol condensation sometimes is done with an OXO reaction. The combined process is called the ALDOX process.

Oxidation of Hydrocarbons

Using air, the oxidation of hydrocarbons generally results in a mixture of oxygenated compounds and is not a useful synthesis of alcohols except under special circumstances. Cyclohexanol may be prepared by air oxidation of cyclohexane inasmuch as only one isomer can result.



The yield of alcohol from normal paraffin oxidation may be improved to a commercially useful level by oxidizing in the presence of boric acid.

$$3\ RH + \frac{3}{2}O_2 + H_3BO_3 \longrightarrow (RO)_3B + 3\ H_2O \qquad (12)$$

$$(RO)_3B + 3\ H_2O \longrightarrow H_3BO_3 + 3\ ROH \qquad (13)$$

A borate ester is formed which is more stable to further oxidation than the free alcohol. This is easily hydrolyzed to recover the alcohol. These alcohols which are predominately secondary are used in surfactant manufacture.

Synthesis from Alkylaluminums

Fundamental work on organoaluminum chemistry by Prof. Karl Ziegler and co-workers at the Max Planck Institute provided the basis for a commercial synthesis of even-carbon-numbered straight chain primary alcohols. These alcohols are identical with products derived from naturally occurring fats. In this process, ethylene is reacted with aluminum triethyl to form a higher alkylaluminum which then is oxidized and hydrolyzed to give the corresponding alcohols.

$$(C_2H_5)_3Al \xrightarrow{CH^2 = CH^2} \qquad (14)$$
$$[CH_3(CH_2CH_2)_nCH_2]_3Al \xrightarrow[(2)\ H_2O]{(1)\ O_2}$$
$$3\ CH_3(CH_2CH_2)_nCH_2OH + Al(OH)_3$$

Commercialization of this route to higher alcohols is the most significant development in this area in recent years.

Synthesis from Natural Products

Many alcohols are prepared by reduction of the corresponding methyl esters which are derived from animal or vegetable fats. These alcohols are straight chain even-carbon-numbered compounds. Tallow and coconut oil are two major raw materials for higher alcohol manufacture.

$$(RCOO)_3C_3H_5 + 3\ CH_3OH \longrightarrow 3\ RCOOCH_3 \qquad (15)$$
$$\textit{Triglyceride}$$
$$+\ CH_2OHCHOHCH_2OH$$

$$RCOOCH_3 + 2\ H_2 \xrightarrow{\text{Catalyst}} RCH_2OH + CH_3OH \qquad (16)$$

The production of ethyl alcohol for beverage, cosmetic, and pharmaceutical products is commonly accomplished by the natural process of fermentation. See **Ethyl Alcohol**; **Methyl Alcohol**; and **Fermentation**. Beer, wine, and whiskey production are extensively covered in the *Foods and*

Food Production Encyclopedia (D.M. and G.D. Considine, Eds.), Van Nostrand Reinhold, New York, 1982.

Additional Reading

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Lagowski, J.J.: *MacMillan Encyclopedia of Chemistry*, Vol. 1, MacMillian Library Reference, New York, NY, 1997.

Parker, S.P.: *McGraw-Hill Concise Encyclopedia of Science and Technology,* McGraw-Hill Companies, New York, NY, 1998.

Ziegler, K. In H. Zeiss: *Organometallic Chemistry,* ACS Monograph **147**, Van Nostrand Reinhold Company, New York, NY, 1960.

ALCOHOLYSIS. If a triglyceride oil is heated with a polyol, such as glycerol or pentaerythritol, mixed partial esters are produced in a reaction known as *alcoholysis*.

ALDEHYDES. The homologous series of aldehydes (like ketones) has the formula $C_nH_{2n}O$. The removal of two hydrogen atoms from an alcohol yields an aldehyde. Thus, two hydrogens taken away from ethyl alcohol $CH_3{\cdot}C(H_2)OH$ yields acetaldehyde CH_3CH_2OH; and two hydrogens removed from propyl alcohol $C_2H_5{\cdot}C(H_2)OH$ yields propaldehyde $C_2H_5{\cdot}CHO$. The trivial names of aldehydes derive from the fatty acid which an aldehyde will yield upon oxidation. Thus, formaldehyde is named from formic acid, the latter being the oxidation product of formaldehyde. Similarly, acetaldehyde is oxidized to acetic acid. Or, the aldehyde may be named after the alcohol from which it may be derived. Thus, formaldehyde, which may be derived from methyl alcohol, may be named methaldehyde; or acetaldehyde may be named ethaldehyde since it may be derived from ethyl alcohol. In still another system, the aldehyde may take its name from the parent hydrocarbon from which it theoretically may be derived. Thus, propa*nal* (not to be confused with propa*nol*) may signify propaldehyde (as a derivative of propane).

Essentially aldehydes exhibit the following properties: (1) with exception of the gaseous formaldehyde, all aldehydes up to C_{11} are neutral, mobile, volatile liquids. Aldehydes above C_{11} are solids under usual ambient conditions; (2) formaldehyde and the liquid aldehydes have an unpleasant, pungent, irritating odor, (3) although the low-carbon aldehydes are soluble in H_2O, the solubility decreases with formula weight, and (4) the high-carbon aldehydes are essentially insoluble in H_2O, but are soluble in alcohol or ether.

The presence of the double bond (carbonyl group C:O) markedly determines the chemical behavior of the aldehydes. The hydrogen atom connected directly to the carbonyl group is not easily displaced. The chemical properties of the aldehydes may be summarized by: (1) they react with alcohols, with elimination of H_2O, to form *acetals*; (2) they combine readily with HCN to form *cyanohydrins*, (3) they react with hydroxylamine to yield *aldoximes*; (4) they react with hydrazine to form *hydrazones*; (5) they can be oxidized into *fatty acids*, which contain the same number of carbons as in the initial aldehyde; (5) they can be reduced readily to form primary alcohols. When benzaldehyde is reduced with sodium amalgam and H_2O, benzyl alcohol $C_6H_5{\cdot}CH_2{\cdot}OH$ is obtained. The latter compound also may be obtained by treating benzaldehyde with a solution of cold KOH in which benzyl alcohol and potassium benzoate are produced. The latter reaction is known as Cannizzaro's reaction.

In the industrial production of higher alcohols (above butyls), aldehydes play the role of an intermediate in a complete process that involves aldol condensation and hydrogenation. In the OXO process, olefins are catalytically converted into aldehydes that contain one more carbon than the olefin in the feedstock. Aldehydes also serve as starting materials in the synthesis of several amino acids. See also **Acetaldehyde**; **Aldol Condensation**; **Benzaldehyde**; and **Furfuraldehyde**.

ALDER, KURT (1902–1958). A German chemist who won the Nobel prize for chemistry along with Otto Diels in 1950 for a project involving a practical method for making ring compounds from chain compounds by forcing them to combine with maleic anhydride. This is known as the Diels-Alder reaction and provided a method for synthesis of complex organic compounds. He had degrees from the Universities of Berlin and Kiel.

ALDOL CONDENSATION. A reaction between aldehydes or aldehydes and ketones that occurs without the elimination of any secondary product and yields β-hydroxycarbonyl compounds. It is distinguished from polymerization by the fact that it occurs between aldehydes and ketones and is not generally reversible. In its simplest form it may be represented by the condensation of two molecules of acetaldehyde to aldol:

$$CH_3 \cdot CHO + CH_3 \cdot CHO \longrightarrow CH_3 \cdot CHOHCH_2 \cdot CHO$$

Weak alkalies and acids are employed to effect the condensation.

Researchers at the University of California, Berkeley, have accomplished acyclic stereocontrol through the aldol condensation. As observed by C.H. Heathcock (*Science*, **214**, 295–400, Oct. 23, 1981), one of the most difficult problems in the synthesis of complex organic compounds is that of controlling the relative stereochemistry, that is, establishing the correct configuration at the various chiral centers as the synthesis is carried out. In recent years, researchers have been attempting to find direct solutions to the problem, particularly in synthesizing acyclic and other conformation-flexible molecules. Heathcock and colleagues have found that aldol condensation, one of the oldest and most familiar organic reactions, can be a very effective tool for achieving stereocontrol.

See also **Aldehydes**; and **Ketones**.

ALDOSES. See **Carbohydrates**.

ALDOSTERONE. See **Steroids**.

ALDOXIMES. See **Hydroxylamine**.

ALEXANDRITE. A variety of chrysoberyl, originally found in the schists of the Ural Mountains. It absorbs yellow and blue light rays to such an extent that it appears emerald green by daylight but columbine-red by artificial light. It is used as a gem, and was named in honor of Czar Alexander II of Russia. See also **Chrysoberyl**.

ALGICIDE. A substance, natural or synthetic, used for destroying or controlling algae. The term is also sometimes used to describe chemicals used for controlling aquatic vegetation, although these materials are more properly classified as aquatic herbicides. See **Herbicides**.

ALGIN. A hydrophilic colloidal polysaccharide obtained from several species of brown algae. The term is used both in reference to the pure substance, alginic acid, extracted from the algae and also to the salts of this acid such as sodium or ammonium alginate, in which forms it is used commercially. The alginates currently find a large number of applications in the paint, rubber, pharmaceutical, food, and other industries. See also **Gums and Mucilages**.

ALIPHATIC COMPOUND. An organic compound that can be regarded as a derivative of methane, CH_4. Most aliphatic compounds are open carbon chains, straight or branched, saturated or unsaturated. Originally, the term was used to denote the higher (fatty) acids of the $C_n\ H_{2n}O_2$ series. The word is derived from the Greek term for oil. See also **Compound (Chemical)**; and **Organic Chemistry**.

ALKALI. A term that was originally applied to the hydroxides and carbonates of sodium and potassium but since has been extended to include the hydroxides and carbonates of the other alkali metals and ammonium. Alkali hydroxides are characterized by ability to form soluble soaps with fatty acids, to restore color to litmus which has been reddened by acids, and to unite with carbon dioxide to form soluble compounds. See also **Acids and Bases**.

ALKALI METALS. The elements of group 1 of the periodic classification. In order of increasing atomic number, they are hydrogen, lithium, sodium, potassium, rubidium, cesium, and francium. With the exception of hydrogen, which is a gas and which frequently imparts a quality of acidity to its compounds, the other members of the group display rather striking similarities of chemical behavior, all reactive with H_2O to form strongly alkaline solutions. The elements in the group, including hydrogen, are characterized by a valence of one, having one electron in an outer shell available for reaction. Because of their chemical similarities, these elements, along with *ammonium* and sometimes magnesium, are considered the sixth group in classical qualitative chemical analysis separations.

ALKALINE EARTHS. The elements of group 2 of the periodic classification. In order of increasing atomic number, they are beryllium, magnesium, calcium, strontium, barium, and radium. The members of the group display rather striking similarities of chemical behavior, including stable oxides and carbonates, with hydroxides that are less alkaline than those of group 1. The elements of the group are characterized by a valence of two, having two electrons in an outer shell available for reaction. Because of their chemical similarities, these elements are considered the fifth group in classical qualitative chemical analysis separations.

ALKALI ROCKS. Igneous rocks which contain a relatively high amount of alkalis in the form of soda amphiboles, *soda* pyroxenes, or felspathoids, are said to be alkaline, or alkalic. Igneous rocks in which the proportions of both lime and alkalis are high, as combined in the minerals, feldspar, hornblende, and augite, are said to be calcalkalic.

ALKALOIDS. The term, alkaloid, which was first proposed by the pharmacist, W. Meissner, in 1819, and means "alkali-like," is applied to basic, nitrogen-containing compounds of plant origin. Two further qualifications usually are added to this definition: (1) the compounds have complex molecular structures; and (2) they manifest significant pharmacological activity. Such compounds occur only in certain genera and families, rarely being universally distributed in larger groups of plants. Many widely distributed bases of plant origin, such as methyltrimethyl-and other open-chain simple alkylamines, the cholines, and the phenylalkylamines, are not classed as alkaloids. Alkaloids usually have a rather complex structure with the nitrogen atom involved in a heterocyclic ring. However, thiamine, a heterocyclic nitrogenous base, is not regarded as an alkaloid mainly because of its almost universal distribution in living matter. Colchicine, on the other hand, is classed as an alkaloid even though it is not basic and its nitrogen atom is not incorporated into a heterocyclic ring. It apparently qualifies as an alkaloid because of its particular pharmacological activity and limited distribution in the plant world.

Over 2000 alkaloids are known and it is estimated that they are present in only 10–15% of all vascular plants. They are rarely found in cryptogamia (exception, ergot alkaloids), gymnosperms, or monocotyledons. They occur abundantly in certain dicotyledons and particularly in the following families: *Apocynaceaae* (dogbane, quebracho, pereiro bark); *Papaveraceae* (poppies, chelidonium); *Papilionaceae* (lupins, butterfly-shaped flowers); *Ranunculaceae* (aconitum, delphinium); *Rubiaceae* (cinchona bark, ipecacuanha); *Rutaceae* (citrus, fagara); and *Solanaceae* (tobacco, deadly nightshade, tomato, potato, thorn apple). Well-characterized alkaloids have been isolated from the roots, seeds, leaves or bark of some 40 plant families. *Papaveraceae* is an unusual family, in that all of its species contain alkaloids.

Brief descriptions in alphabetical order of alkaloids of commercial or medical importance or of societal concern (alkaloid narcotics) are given later in this entry. See also **Amphetamine**; **Morphine**; and **Pyridine and Derivatives**.

The nomenclature of alkaloids has not been systemized, both because of the complexity of the compounds and for historical reasons. The two commonly used systems classify alkaloids either according to the plant genera in which they occur, or on the basis of similarity of molecular structure. Important classes of alkaloids containing generically related members are the aconitum, cinchona, ephedra, lupin, opium, rauwolfia, senecio, solanum, and strychnos alkaloids. Chemically derived alkaloid names are based upon the skeletal feature which members of a group possess in common. Thus, indole alkaloids (e.g., psilocybin, the active principle of Mexican hallucinogenic mushrooms) contain an indole or modified indole nucleus, and pyrrolidine alkaloids (e.g., hygrine) contain the pyrrolidine ring system. Other examples of this type of classification include the pyridine, quinoline, isoquinoline, imidazole, pyridine-pyrrolidine, and piperidine-pyrrolidine type alkaloids. Several alkaloids are summarized along these general terms in Table 1.

The beginning of alkaloid chemistry is usually considered to be 1805 when F.W. Sertürner first isolated morphine. He prepared several salts of morphine and demonstrated that it was the principle responsible for the physiological effect of opium. Alkaloid research has continued to date, but because most likely plant sources have been investigated and because a large number of synthetic drugs serve medical and other needs more effectively, the greatest emphasis has been placed upon the synthetics.

TABLE 1. GENERAL CLASSIFICATION OF ALKALOIDS

General Class	Examples
Derivatives of aryl-substituted amines	Adrenaline, amphetamine, ephedrine, phenylephrine tyramine
Derivatives of pyrrole	Carpaine, hygrine, nicotine
Derivatives of imidazole	Pilocarpine
Derivatives of pyridine and piperidine	Anabasine, coniine, ricinine
Containing fusion of two piperidine rings	Isopelletierine, pseudopelletierine
Pyrrole rings fused with other rings	Gelsemine, physostigmine, vasicine, yohimbine
Aporphone alkaloids	Apomorphine corydine, isothebaine
Berberine alkaloids	Berberine, emetine
Bis-benzylisoquinoline alkaloids	Bebeering, trilobine
Cinchona alkaloids	Cinchonine, quinidine, quinine
Cryptopine alkaloids	Cryptopine, protopine
Isoquinoline alkaloids	Anhalidine, pellotine, sarsoline
Lupine alkaloids	Lupanine, sparteine
Morphine and related alkaloids	Codeine, morphine, thebaine
Papaverine alkaloids	Codamine, homolaudanosine, papeverine
Phthalide isoquinoline alkaloids (also known as narcotine alkaloids)	Hydrastine, narceine, narcotine
Quinoline alkaloids	Dictamine, galipoline, lycorine
Tropine alkaloids	Atropine, cocaine, ecgonine, scopolamine, tropine
Other alkaloids	Brucine, sclanidine, strychnine

Sometimes, there is confusion between alkaloids and narcotics. It should be stressed that all alkaloids are not narcotics; and all narcotics are not alkaloids. A narcotic has the general definition of a drug that produces sleep or stupor, and also relieves pain. Many alkaloids do not meet these specifications.

The molecular complexity of the alkaloids is demonstrated by Fig. 1. Alkaloids react as bases to form salts. The salts used especially for crystallization purposes are the hydrochlorides, sulfates, and oxalates, which are generally soluble in water or alcohol, insoluble in ether, chloroform, carbon tetrachloride, or amyl alcohol. Alkaloid salts unite with mercury, gold, and platinum chlorides. Free alkaloids lack characteristic color reactions but react with certain reagents, as follows, with (1) iodine in potassium iodide solution, forming chocolate brown precipitate; (2) mercuric iodide in potassium iodide solution (potassium mercuriiodide), forming precipitate; (3) potassium iodobismuthate, forming orange-red precipitate; (4) bromine-saturated concentrated hydrobromic acid forming yellow precipitate; (5) tannic acid, forming precipitate; (6) molybdophosphoric acid, forming precipitate; (7) tungstophosphoric acid, forming precipitate; (8) gold(III) chloride, forming crystalline precipitate of characteristic melting point; (9) platinum(IV) chloride, forming crystalline precipitate of characteristic melting point; (10) picric acid, forming precipitate; (11) perchloric acid, forming precipitate. Many alkaloids form more or less characteristic colors with acids, solutions of acidic salts, etc.

The function of alkaloids in the source plant has not been fully explained. Some authorities simply regard them as by-products of the plant metabolism. Others conceive of alkaloids as reservoirs for protein synthesis; as protective materials discouraging animal or insect attacks; as plant stimulants or regulators in such activities as growth, metabolism, and reproduction; as detoxifying agents, which render harmless (by processes such as methylation, condensation, and ring closure) substances whose accumulation might otherwise cause damage to the plant. While these theories are of interest, it is also of interest to observe that from 85–90% of all plants manage well without the presence of alkaloids in their structures.

Adrenaline®. See **Epinephrine** later in this entry.

Atropine, also known as daturine, $C_{17}H_{23}NO_3$ (see structural formula in accompanying diagram), white, crystalline substance, optically inactive, but usually contains levorotatory hyoscyamine. Compound is soluble in alcohol, ether, chloroform, and glycerol; slightly soluble in water; mp 114–116°C. Atropine is prepared by extraction from *Datura stramonium*, or synthesized. The compound is toxic and allergenic. Atropine is used in medicine and is an antidote for cholinesterase-inhibiting compounds, such as organophosphorus insecticides and certain nerve gases. Atropine is commonly offered as the sulfate. Atropine is used in connection with the treatment of disturbances of cardiac rhythm and conductance, notably in the therapy of sinus bradycardia and sick sinus syndrome. Atropine is also used in some cases of heart block. In particularly high doses, atropine may induce ventricular tachycardia in an ischemic myocardium. Atropine is frequently one of several components in brand name prescription drugs.

Caffeine, also known as theine, or methyltheobromine, 1,2,7-trimethyl xanthine (see structural formula in accompanying diagram), white, fleecy or long, flexible crystals. Caffeine effloresces in air and commences losing water at 80°C. Soluble in chloroform, slightly soluble in water and alcohol, very slightly soluble in ether, mp 236.8°C, odorless, bitter taste. Solutions are neutral to litmus paper.

Caffeine is derived by extraction of coffee beans, tea leaves, and kola nuts. It is also prepared synthetically. Much of the caffeine of commerce is a by-product of decaffeinized coffee manufacture. The compound is purified by a series of recrystallizations. Caffeine finds use in medicine and in soft drinks. Caffeine is also available as the hydrobromide and as sodium benzoate, which is a mixture of caffeine and sodium benzoate, containing 47–50% anhydrous caffeine and 50–53% sodium benzoate. This mixture is more soluble in water than pure caffeine. A number of nonprescription (pain relief) drugs contain caffeine as one of several ingredients. Caffeine is a known cardiac stimulant and in some persons who consume significant amounts, caffeine can produce ventricular premature beats.

Cocaine (also known as methylbenzoylepgonine), $C_{17}H_{21}NO_4$, is a colorless-to-white crystalline substance, usually reduced to powder. Cocaine is soluble in alcohol, chloroform, and ether, slightly soluble in water, giving a solution slightly alkaline to litmus. The hydrochloride is levorotatory, mp 98°C. Cocaine is derived by extraction of the leaves of coca (*Erythroxylon*) with sodium carbonate solution, followed by treatment with dilute acid and extraction with ether. The solvent is evaporated after which the substance is re-dissolved and subsequently crystallized. Cocaine also is prepared synthetically from the alkaloid ecgonine. Cocaine is *highly toxic* and *habit-forming*. While there are some medical uses of cocaine, usage must always be under the direction of a physician. It is classified as a narcotic in most countries. Society's major concern with cocaine is its use (increasing in recent years) as a narcotic.

Cocaine has been known as a very dangerous material since the early 1900s. When use of it as a narcotic increased during the early 1970s, serious misconceptions concerning its "safety" as compared with many other narcotics led and continue to lead to many deaths from its use.

Addicts use cocaine intravenously or by snorting the powder. After intravenous injections, coma and respiratory depression can occur rapidly. It has been reported that fatalities associated with snorting usually occur shortly after the abrupt onset of major motor seizures, which may develop within minutes to an hour after several nasal ingestions. Similar results occur if the substance is taken by mouth. Treatment is directed toward ventilatory support and control of seizures—although in many instances a victim may not be discovered in time to prevent death. It is interesting to note that cocaine smugglers, who have placed cocaine-filled condoms in their rectum or alimentary tract, have died (Suarez et al., 1977). The structural formula of cocaine is given in Fig. 1.

Codeine, also known as methylmorphine, $C_{18}H_{21}NO_3 \cdot H_2O$, is a colorless white crystalline substance, mp 154.9°C, slightly soluble in water, soluble in alcohol and chloroform, effloresces slowly in dry air. Codeine is derived from opium by extraction or by the methylation of morphine. For medical use, codeine is usually offered as the dichloride, phosphate, or sulfate. Codeine is *habit forming*. Codeine is known to exacerbate *urticaria* (familiarly known as *hives*). Since codeine is incorporated in numerous prescription medicines for headache, heartburn, fatigue, coughing, and relief of aches and pains, persons with a history of urticaria should make this fact known to their physician. Codeine is sometimes used in cases of acute *pericarditis* to relieve severe chest pains in early phases of disease. Codeine is sometimes used in drug therapy of renal (kidney) diseases.

Colchicine, an alkaloid plant hormone, $C_{22}H_{25}NO_6$, is yellow crystalline or powdered, nearly odorless, mp 135–150°C, soluble in water, alcohol,

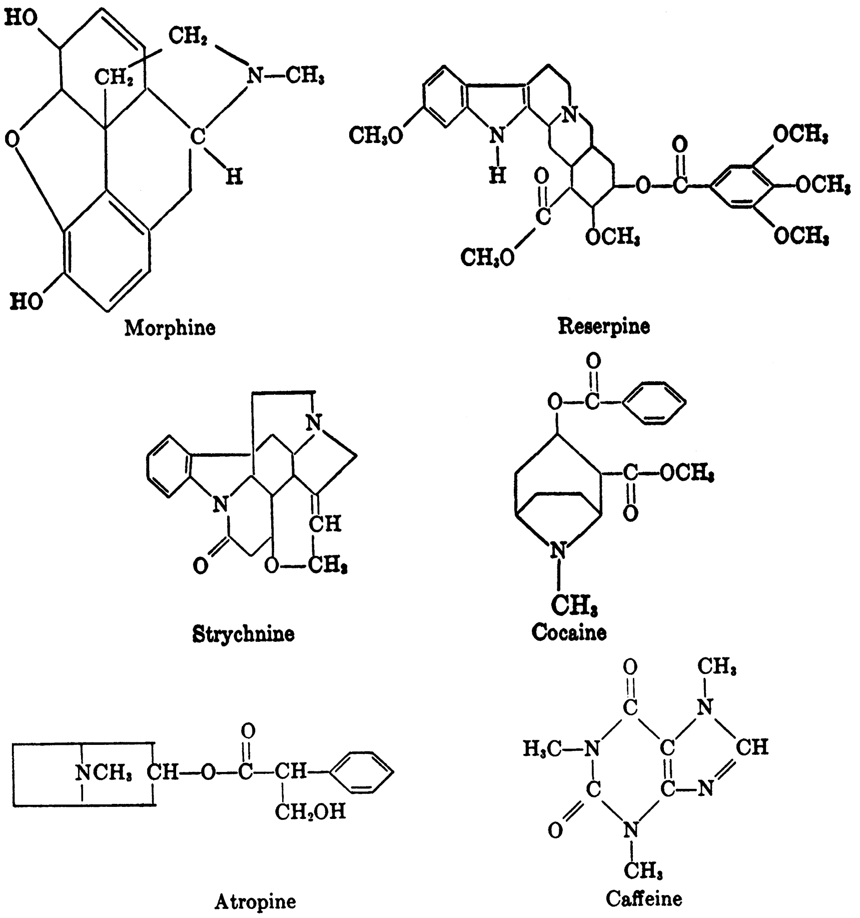

Fig. 1. Structures of representative alkaloids. The carbon atoms in the rings and the hydrogen atoms attached to them are not designated by letter symbols. However, there is understood to be a carbon atom at each corner (except for the cross-over in the structure of morphine) and each carbon atom has four bonds, so that any bonds not shown or represented by attached groups are joined to hydrogen atoms

and chloroform, moderately soluble in ether. Solutions are levorotatory and deteriorate under light. The substance is highly toxic (0.02 gram may be fatal if ingested). Colchicine is extracted from the plant *Colchicum autumnale* after which it is crystallized. The compound also has been synthesized. Biologists have used colchicine to induce chromosome doubling in plants. Colchicine finds a number of uses in medicine.

Although colchicine has been known for many years, interest in the drug has been revitalized in recent years as the result of the discovery that it interferes with cell division by destroying the spindle mechanism. The two chromatids, which represent one chromosome at the metaphase stage, fail to separate and do not migrate to the poles (ends) of the cell. Each chromatid becomes a chromosome *in situ*. The entire group of new chromosomes now forms a resting nucleus and the next cell division reveals twice as many chromosomes as before. The cell has changed from the diploid to the tetraploid condition. Applied to germinating seeds or growing stem tips in concentrations of about 1 gram in 10,000 cubic centimeters of water for 4 or 5 days, colchicine may thus double the chromosome number of many or all of the cells, producing a tetraploid plant or shoot. Offspring from such plants may be wholly tetraploid and breed true. Tetraploid plants are larger than diploid plants and often more valuable. The alkaloid has also been used to double the chromosome number of sterile hybrids produced by crossing widely separated species of plants. Such plants, after colchicine treatment, contain in each cell two complete diploid sets of chromosomes, one from each of the parent species, and become fertile, pure-breeding hybrid species.

In medicine, colchicine is probably best known for its use in connection with the treatment of gout. Acute attacks of gout are characteristically and specifically aborted by colchicine. The response noted after administration of the drug also can be useful in diagnosing gout cases where synovial fluid cannot be aspirated and examined for the presence of typical urate crystals. However, colchicine does not affect the course of acute synovitis in rheumatoid arthritis.

Kaplan (1960) observed that colchicine may produce objective improvement in the periarthritis associated with *sarcoidosis* (presence of noncaseating granulomas in tissue). Colchicine is sometimes used in the treatment of *scleroderma* (deposition of fibrous connective tissues in skin or other organs); it may assist in preventing attacks of Mediterranean fever; and it is sometimes used as part of drug therapy for some renal (kidney) diseases.

Colchicine can cause diarrhea as the result of mucosal damage and it has been established that colchicine interferes with the absorption of vitamin B_{12}.

Emetine, an alkaloid from ipecac, $C_{29}H_{40}O_4N_2$, is a white powder, mp 74°C, with a very bitter taste. The substance is soluble in alcohol and ether, slightly soluble in water. Emetine darkens upon exposure to light. The compound is derived by extraction from the root of *Cephalis ipecacuanha* (ipecac). It is also made synthetically. Medically, ipecac is useful as an emetic (induces vomiting) for emergency use in the treatment of drug overdosage and in certain cases of poisoning. Ipecac should not be administered to persons in an unconscious state. It should be noted that emesis is not the proper treatment in all cases of potential poisoning. It should not be induced when such substances as petroleum distillates, strong alkali, acids, or strychnine are ingested.

Ephedrine, 1-phenyl-2-methylaminopropanol, $C_6H_5CH(OH)CH(NHCH_3)CH_3$, is a white-to-colorless granular substance, unctuous (greasy) to the touch, and hygroscopic. The compound gradually decomposes upon exposure to light. Soluble in water, alcohol, ether, chloroform, and oils, mp 33–40°C, by 255°C, and decomposes above this temperature. Ephedrine is isolated from stems or leaves of *Ephedra*, especially Ma huang (found in China and India). Medically, it is usually offered as the hydrochloride. In the treatment of bronchial asthma, ephedrine is known as a *beta agonist*. Compounds of this type reduce obstruction by activating the enzyme adenylate cyclase. This increases intracellular concentrations of cAMP (cyclic 3′5′-adenosine monophosphate) in bronchial smooth muscle and mast cells. Ephedrine is most useful for the treatment of mild asthma. In severe asthma, ephedrine rarely maintains completely normal airway dynamics over long periods. Ephedrine also has been used in the treatment of cerebral transient ischemic attacks, particularly with patients with vertabrobasilar artery insufficiency who have symptoms associated with relatively low blood pressure, or with postural changes in blood pressure. Ephedrine sulfate also has been used in drug therapy in connection with urticaria (hives).

Epinephrine, a hormone having a benzenoid structure, $C_9H_{13}O_3N$, also called adrenaline. It can be obtained by extraction from the adrenal glands of cattle and also prepared synthetically. Its effect on body metabolism is pronounced, causing an increase in blood pressure and rate of heartbeat. Under normal conditions, its rate of release into the system is constant, but emotional stresses, such as fear or anger rapidly increase the output and result in temporarily heightened metabolic activity. Epinephrine is used for the symptomatic treatment of bronchial asthma and reversible bronchospasm associated with chronic bronchitis and emphysema. The drug acts on both alpha and beta receptor sites. Beta stimulation provides bronchodilator action by relaxing bronchial muscle. Alpha stimulation increases vital capacity by reducing congestion of the bronchial mucosa and by constricting pulmonary vessels.

Epinephrine is also used in the management of anesthetic procedures in connection with noncardiac surgery of patients with active ischemic heart disease. The drug is useful in the treatment of severe urticarial (hives) attacks, especially those accompanied by angioedema.

Epinephrine has numerous effects on intermediary metabolism. Among these are promotion of hepatic glycogenolysis, inhibition of hepatic gluconeogenesis, and inhibition of insulin release. The drug also promotes the release of free fatty acids from triglyceride stores in adipose tissues. Epinephrine produces numerous cardiovascular effects. Epinephrine is particularly useful in treating conditions of immediate hypersensitivity—interactions between antigen and antibody. These mechanisms cause attacks of anaphylaxis, hay fever, hives and allergic asthma. Anaphylaxis can occur after bee and wasp stings, venoms, etc. Although the mechanism is not fully understood, epinephrine can play a lifesaving role in the treatment of acute systemic anaphylaxis.

In some instances, epinephrine can be a cause of a blood condition involving the leukocytes and known as neutrophilia. In very rare cases, an intramuscular injection of epinephrine can be a cause of clostridial myonecrosis (gas gangrene).

Heroin, diacetylmorphine $C_{17}H_{17}NO(C_2H_3O_2)_2$, is a white, essentially odorless, crystalline powder with bitter taste, soluble in alcohol, mp 173°C. Heroin is derived by the acetylization of morphine. The substance is highly toxic and is a habit-forming narcotic. One-sixth grain (0.0108 gram) can be fatal. Although emergency facility personnel in some areas during recent years have come to regard heroin overdosage as approaching epidemic statistics, it is nevertheless estimated that the majority of persons with heroin overdose die before reaching a hospital. The initial crisis of an overdose is a severe respiratory depression and sometimes *apnea* (cessation of breathing). In emergency situations, the victim may be ventilated with a self-inflating resuscitative bag with delivery of 100% oxygen. Then, an endotracheal tube attached to a mechanical ventilator may be inserted. Naloxone (*Narcan*®), a narcotic antagonist, then may be administered intraveneously, often with repeated dosages over short intervals, until an improvement is noted in the respiratory rate or sensorial level of the victim. If a victim does not respond, this is usually indication that the situation is not opiate-related, or that other drugs also have been taken. Inasmuch as the antagonizing action of naloxone persists for only a few hours, a heroin overdose patient should be observed in the hospital for an indeterminate period. In heroin overdose cases, pulmonary edema (as the result of altered capillary permeability) may occur. This is directly associated with the overdose and not with subsequent treatment. Aside from severe overdose, the drug causes or contributes to a number of ailments. These include chronic renal (kidney) failure and nephritic syndrome. Septic arthritis, caused by *Pseudomonas* and *Serratia* infections, is sometimes found as the result of intravenous heroin abuse. Drug-induced immune platelet destruction also may occur.

Morphine. See separate entry on **Morphine**.

Neo-Synephrine®. See **Phenylephrine hydrochloride** later in this entry.

Nicotine, beta-pyridyl-alpha-N-methylpyrrolidine, $C_5H_4NC_4H_7NCH_3$, is a thick, water-white levorotatory oil that turns brown upon exposure to air. The compound is hygroscopic, soluble in alcohol, chloroform, ether, kerosene, water, and oils, bp 247°C, at which point it decomposes. Specific gravity is 1.00924. Nicotine is combustible with an auto-ignition temperature of 243°C. Nicotine is derived by distilling tobacco with milk of lime and extracting with ether. Nicotine is used in medicine, as an insecticide, and as a tanning agent. Nicotine is commercially available as the dihydrochloride, salicylate, sulfate, and bitartrate. Nicotinic acid (pyridine-3-carboxylic acid) is a vitamin in the B complex. See also **Vitamin**.

PhenylephrineHydrochloride

l-1-(meta-hydroxyphenyl-2-methyl-) aminoethanol hydrochloride, $HOC_6H_4CH(OH)CH_2NHCN_3 \cdot HCl$, white or nearly white crystalline substance, odorless, bitter taste. Solutions are acid to litmus paper, freely soluble in water and in alcohol, mp 140–145°C. Levorotatory in solution. Phenylephrine hydrochloride is used medically as a vasoconstrictor and pressor drug. It is chemically related to epinephrine and ephedrine. Actions are usually longer lasting than the latter two drugs. The action of phenylephrine hydrochloride contrasts sharply with epinephrine and ephedrine, in that its action on the heart is to slow the rate and to increase the stroke output, inducing no disturbance in the rhythm of the pulse. In therapeutic doses, it produces little if any stimulation of either the spinal cord or cerebrum. The drug is intended for the maintenance of an adequate level of blood pressure during spinal and inhalation anesthesia and for the treatment of vascular failure in shock, shock-like states, and drug-induced hypotension, or hypersensitivity. It is also used to overcome paroxysmal supraventricular tachycardia, to prolong spinal anesthesia, and as a vasoconstrictor in regional analgesia. Caution is required in the administration of phenylephrine hydrochloride to elderly persons, or to patients with hyperthyroidism, bradycardia, partial heart block, myocardial disease, or severe arteriosclerosis. The brand name *Neo-Synephrine*® is also used to designate another product (nose drops) which does not contain phenylephrine hydrochloride. The nose drops contain xylometazoline hydrochloride.

Quinine, $C_{20}H_{24}N_2O_2 \cdot H_2O$, a bulky, white, amorphous powder or crystalline substance, with very bitter taste. It is odorless and levorotatory. Soluble in alcohol, ether, chloroform, carbon disulfide, oils, glycerol, and acids; very slightly soluble in water. Quinine is derived from finely ground cinchona bark mixed with lime. This mixture is extracted with hot, high-boiling paraffin oil. The solution is filtered, shaken with dilute sulfuric acid and then neutralized while hot with sodium carbonate. Upon cooling, quinine sulfate crystallizes out. Pure quinine is obtained by treating the sulfate with ammonia. In addition to medical uses, quinine and its salts are used in soft drinks and other beverages.

Quinine derivatives are used in therapy for mytonic dystrophy (usually weakness and wasting of facial muscles); in the treatment of certain renal (kidney) diseases. Quinine and derivatives are best known for their use in connection with malaria. Acute attacks of malaria are usually treated with oral chloroquine phosphate. The drug is given intramuscularly to patients who cannot tolerate oral medication. Combined therapy is indicated for treating *P. falciparum* infections, using quinine sulfate and pyrimethamine. A weekly oral dose of chloroquinone phosphate is frequently prescribed for persons who travel in malarial regions. The drug is taken one week prior to travel into such areas and continued for six weeks after leaving the region. Chloroquine phosphate has not proved fully satisfactory in the treatment of babesiosis, a malaria-like illness caused by a parasite.

Strychnine, $C_{21}H_{24}ON_2$, hard, white crystals or powder of a bitter taste. Soluble in chloroform, slightly soluble in alcohol and benzene, slightly soluble in water and ether, mp 268–290°C, bp 270°C (5 millimeters pressure). Strychnine is obtained by extraction of the seeds of *Nux vomica* with acetic acid, followed by filtration, precipitation by an alkali, followed by final filtration. The compound is highly toxic by ingestion and inhalation. The phosphate finds limited medical use. Strychnine is also used in rodent poisons. Strychnine acts as a powerful stimulant to the central nervous system. At one time, strychnine was used in a very carefully controlled way in the treatment of some cardiac disorders. Acute strychnine poisoning resembles fully developed generalized tetanus.

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ALKALOSIS. A condition of excess alkalinity (or depletion of acid) in the body, in which the acid-base balance of the body is upset. The hydrogen ion concentration of the blood drops below the normal level, increasing the pH value of the blood above the normal 7.4. The condition can result from the ingestion or formation in the body of an excess of alkali, or of loss of acid. Common causes of alkalosis include: (1) overbreathing (hyperventilation), where a person may breathe too deeply for too long a period, consequently washing out carbon dioxide from the blood, (2) ingestion of excessive alkali, as for example an overdosage of sodium bicarbonate possibly taken for the relief of gastric distress, and (3) excessive vomiting, which leads to loss of chloride and retention of sodium ions. The usual, mild symptoms of alkalosis are restlessness, possible numbness or tingling of the extremities (hands and feet), and generally increased muscular irritability. Only in extreme cases, tetany (muscle spasm) and convulsions may be evidenced.

See also **Acid-Base Regulation (Blood)**; **Blood**; and **Potassium and Sodium (In Biological Systems)**.

ALKANE. One of the group of hydrocarbons of the paraffin series, e.g., methane, ethane, and propane. See also **Organic Chemistry**.

ALKENE. One of a group of hydrocarbons having one double bond and the type formula $C_n\ H_{2n}$, e.g., ethylene and propylene. See also **Organic Chemistry**.

ALKYD. See **Paint and Finish Removers**.

ALKYD RESINS. In spite of challenges from many new coating resins developed over the years, alkyd resins as a family have maintained a prominent position for two principal reasons, their high versatility and low cost.

Fundamental Reactions and Resin Structure

The main reactions involved in alkyd resin synthesis are polycondensation by esterification and ester interchange. Figure 1 uses the following symbols to represent the basic components of an alkyd resin.

As Figure 1 implies, there is usually some residual acidity as well as free hydroxyl groups left in the resin molecules.

Classification of Alkyd Resins

Alkyd resins are usually referred to by a brief description based on certain classification schemes. From the classification the general properties of the resin become immediately apparent. Classification is based on the nature of the fatty acid and oil length.

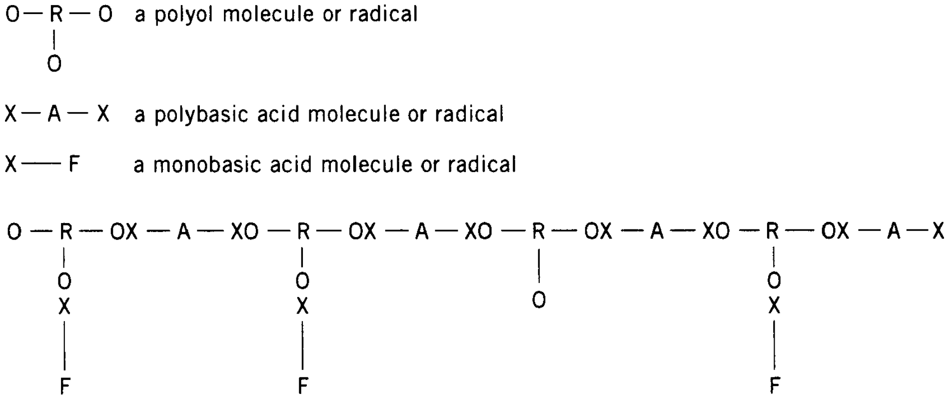

Fig. 1. Schematic representation of an alkyd resin molecule

TABLE 1. PROPERTY CHANGES WITH OIL LENGTH OF ALKYD RESINS[A]

Property	Oil length Long	 Medium	 Short
requirement of aromatic/polar solvents	———	———	——→
compatibility with other film-formers	———	———	——→
viscosity	———	———	——→
ease of brushing	←——	———	———
air dry time, set-to-touch	←——	———	———
through-dry	←———		———→
film hardness	←———		———→
gloss	———	———	——→
gloss retention	———	———	——→
color retention	———	———	——→
exterior durability	←———		———→

[a] Primarily drying-type alkyds.

Oil Length-Resin Property Relationship

The oil length of an alkyd resin has profound effects on the properties of the resin (Table 1).

Alkyd Ingredients

For each of the three principal components of alkyd resins, the polybasic acids, the polyols, and the monobasic acids, there is a large variety to be chosen from. The selection of each of these ingredients affects the properties of the resin and may affect the choice of manufacturing processes. Thus, to both the resin manufacturers and the users, the selection of the proper ingredients is a significant decision.

Polybasic Acids and Anhydrides. The principal polybasic acids used in alkyd preparation include phthalic anhydride (mol wt 148, eq wt 74), isophthalic acid (mol wt 166, eq wt 83), maleic anhydride (mol wt 98, eq wt 49), fumaric acid (mol wt 116, eq wt 58), adipic acid (mol wt 146, eq wt 73), azelaic acid (mol wt 160, eq wt 80), sebacic acid (mol wt 174, eq wt 87), chlorendic anhydride (mol wt 371, eq wt 185.5), and trimellitic anhydride (mol wt 192, eq wt 64).

Polyhydric Alcohols. The principal types of polyol used in alkyd synthesis are shown in Table 2.

Monobasic Acids. The overwhelming majority of monobasic acids used in alkyd resins are long-chain fatty acids of natural occurrence. They may be used in the form of oil or free fatty acid. Free fatty acids are usually available and classified by their origin, *viz*, soya fatty acids, linseed fatty acids, coconut fatty acids, etc. Fats and oils commonly used in alkyd resins include castor oil, coconut oil, cottonseed oil, linseed oil, oiticica oil, peanut oil, rapeseed oil, safflower oil, soyabean oil, sunflowerseed oil, and tung oil.

The drying property of fats and oils is related to their degree of unsaturation, and hence, to iodine values.

Linolenic acid is responsible for the high yellowing tendency of alkyds based on linseed oil fatty acids. Alkyds made with nondrying oils or their fatty acids have excellent color and gloss stability. They are frequently the choice for white industrial baking enamels and lacquers.

TABLE 2. POLYOLS FOR ALKYD SYNTHESIS

Type	Mol wt	Eq wt
pentaerythritol	136	34
glycerol	92	31[a]
trimethylolpropane	134	44.7
trimethylolethane	120	40
ethylene glycol	62	31
neopentyl glycol	104	52

[a] Because glycerol is usually supplied at 99% purity (1% moisture), its eq wt is commonly assumed to be 31 in recipe calculations.

The Concept of Functionality and Gelation

The concept of functionality and its relationship to polymer formation was greatly expanded the theoretical consideration and mathematical treatment of polycondensation systems. Thus if a dibasic acid and a diol react to form a polyester, assuming there is no possibility of other side reactions to complicate the issue, only linear polymer molecules are formed. When the reactants are present in stoichiometric amounts, the average degree of polymerization, $\overline{x}_n$ follows the equation:

$$\overline{x}_n = 1/(1-p) \tag{1}$$

where p is the fractional extent of reaction. Thus when the reaction is driven to completion, theoretically, the molecular weight approaches infinity and the whole mass forms one giant polymer molecule. Although the material should theoretically still be soluble and fusible the molecular weight would be so high that it would not be processible by any of the existing methods. For all practical purposes it is a gel; this is the sole example of difunctional monomers being polymerized to gelation.

The functionality of the system, f, is the sum of all of the functional groups, i.e., equivalents, divided by the total number of moles of the reactants present in the system. Thus, in the above equimolar reaction system,

$$f = (1 \times 2 + 1 \times 2)/(1+1) = 2 \tag{2}$$

Microgel Formation and Molecular Weight Distribution

The behavior of alkyd resin reactions often deviates from that predicted by the theory of Flory. To explain this, a mechanism of microgel formation by some of the alkyd molecules at relatively early stage of the reaction was proposed. The microgel particles are dispersed and stabilized by smaller molecules in the remaining reaction mixture. As polyesterification proceeds, more microgel particles are formed, until finally a point is reached where they can no longer be kept separated. The microgel particles then coalese or flocculate, phase inversion occurs, and the entire reaction mass gels. The drying capability of an alkyd resin comes primarily from the microgel fraction. For example, when the highest molecular weight fraction representing about 20% of the total was removed through fractionation, a residual linoleic alkyd lost all ability to air dry to a hard film.

Principles for the Designing of Alkyd Resins

The process of alkyd resin designing should begin with the question "What are the intended applications of the resin?" The application dictates property requirements, such as solubility, viscosity, drying characteristics, compatibility, film hardness, film flexibility, acid value water resistance, chemical resistance, and environmental endurance With the targets in mind, a selection of oil length and a preliminary list of alternative choices of ingredients can then be made. For commercial production, the raw material list is screened based considerations of material cost, availability, yield, impact on processing cost, and potential hazard to health, safety, and the environmen. The list may be further narrowed by limitations imposed by the production equipment or other considerations. Once the oil length and ingredients are chosen, the first draft of a detailed formulation for the resin can be made.

A simple molecular approach is favored by some alkyd chemists for deriving a starting formulation. The basic premise of this approach is that when the total number of moles of the polyols is equal to or slightly larger than that of the dibasic acids, and the hydroxyl groups are present in an empirically prescribed excess amount, the probability of gelation is very small. Table 3 lists the empirical requirements for excess hydroxyl groups at various oil (fatty acid) lengths of the alkyd.

Chemical Procedures for Alkyd Resin Synthesis

Different chemical procedures may be used for the synthesis of alkyd resins. The choice is usually dictated by the selection of the starting ingredients. Procedures include the alcoholysis process, the fatty acid process, the fatty acid–oil process, and the acidolysis process.

Alkyd Resin Production Processes

Depending on the requirements of the chemical procedures, the processing method may be varied with different mechanical arrangements to remove the by-product, water, in order to drive the esterification reaction toward completion. Methods include the fusion process and the solvent process.

Process Control. The progress of the alkyd reaction is usually monitored by periodic determinations of the acid number and the solution viscosity of samples taken from the reactor. The frequency of sampling is commonly every half-hour.

Safety and Environmental Precautions

The manufacturing of alkyd resins involves a wide variety of organic ingredients. Whereas most of them are relatively mild and of low toxicity, some, such as phthalic anhydride, maleic anhydride, solvents, and many of the vinyl (especially acrylic) monomers, are known irritants or skin sensitizers and are poisonous to humans. The hazard potential of the chemicals should be determined by consulting the Material Safety Data Sheets provided by the suppliers, and recommended safety precautions in handling the materials should be practiced.

With the ever-increasing awareness of the need of environment protection, the emission of solvent vapors and organic fumes into the atmosphere should be prevented by treating the exhaust through a proper scrubber. The solvent used for cleaning the reactor is usually consumed as part of the thinning solvent. Aqueous effluent should be properly treated before discharge.

Modification of Alkyd Resins by Blending With Other Polymers

One of the important attributes of alkyds is their good compatibility with a wide variety of other coating polymers. This good compatibility comes from the relatively low molecular weight of the alkyds, and the fact that the resin structure contains, on the one hand, a relatively polar and aromatic backbone, and, on the other hand, many aliphatic side chains with low polarity. An alkyd resin in a blend with another coating polymer may serve as a modifier for the other film-former, or it may be the principal film-former and the other polymer may serve as the modifier for the alkyd to enhance certain properties. Examples of compatible blends follow.

Nitrocellulose-based lacquers often contain short or medium oil alkyds to improve flexibility and adhesion. The principal applications are furniture coatings, top lacquer for printed paper, and automotive refinishing primers.

Amino resins are probably the most important modifiers for alkyd resins. Many industrial baking enamels, such as those for appliances, coil coatings, and automotive finishes (especially refinishing enamels), are based on alkyd-amino resin blends. Some of the so-called catalyzed lacquers for finishing wood substrate require very low bake or no bake at all.

Chlorinated rubber is often used in combination with medium oil drying-type alkyds. The principal applications are highway traffic paint, concrete floor, and swimming pool paints.

Vinyl resins, i.e., copolymers of vinyl chloride and vinyl acetate which contain hydroxyl groups from the partial hydrolysis of vinyl acetate or carboxyl groups, e.g., from copolymerized maleic anhydride, may be formulated with alkyd resins to improve their application properties and adhesion. The blends are primarily used in making marine top-coat paints.

Synthetic latex house paints sometimes contain emulsified long oil or very long oil drying alkyds to improve adhesion to chalky painted surfaces.

Silicone resins with high phenyl contents may be used with medium or short oil alkyds as blends in air-dried or baked coatings to improve heat or weather resistance; the alkyd component contributes to adhesion and flexibility. Applications include insulation varnishes, heat-resistant paints, and marine coatings.

TABLE 3. EXCESS HYDROXYL CONTENT REQUIRED IN ALKYD FORMULATIONS

Oil length, fatty acid, %[a]	Excess OH based on diacid equivalents, %
62 or more	0
59–62	5
57–59	10
53–57	18
48–53	25
38–48	30
29–38	32

[a] Based on C-18 fatty acids with average eq wt of 280. If the average eq wt of the monobasic acids is significantly different, adjustment is necessary.

Chemically Modified Alkyd Resins

Although blending with other coating resins provides a variety of ways to improve the performance of alkyds, or of the other resins, chemically combining the desired modifier into the alkyd structure eliminates compatibility problems and gives a more uniform product. Several such chemical modifications of the alkyd resins have gained commercial importance. They include vinylated alkyds, silicone alkyds, urethane alkyds, phenolic alkyds, and polyamide alkyds.

High Solids Alkyds

There has been a strong trend in recent years to increase the solids content of all coating materials, including alkyds, to reduce solvent vapor emission. In order to raise solids and still maintain a manageable viscosity, the molecular weight of the resin must be reduced. Consequently, film integrity must be developed through further chain extension or cross-linking of the resin molecules during the "drying" step. A high cross-linking density necessitated by the lower molecular weight of the resin builds high stress in the film and causes it to be prone to cracking. Therefore, adequate flexibility should be designed into the resin structure. Chain extension and cross-linking of high solids alkyd resins are typically achieved by the use of polyisocyanato oligomers or amino resins.

Water-Reducible Alkyds

Replacing solvent-borne coatings with water-borne coatings not only reduces solvent vapor emission, but also improves the safety against the fire and health hazards of organic solvents. Alkyd resins may be made water-reducible either by converting the resin into an emulsion form or by incorporating "water-soluble" groups in the molecules.

Economic Aspects

Alkyd resins, as a family, have remained the workhorse of the coatings industry for decades. The top alkyd resin manufacturers in the United States are Cargill, Reichhold, a subsidiary of Dainippon Ink & Chemicals, Inc., and Spencer Kellog, now a part of NL Industries, Inc.

Future Prospects. Because of the efforts of the coatings industry to reduce solvent emission, there has been a clear gradual decline in the market share of alkyds as a group relative to all synthetic coating resins. However, their versatility and low cost will undoubtedly maintain them as significant players in the coatings arena. Alkyds are much more amenable to development of higher solids compositions than most other coating resins. Great strides in the development of water-borne types have also been made in recent years. Another good reason to remain optimistic about alkyds for the future is that a significant portion of their raw material, fatty acids, is renewable.

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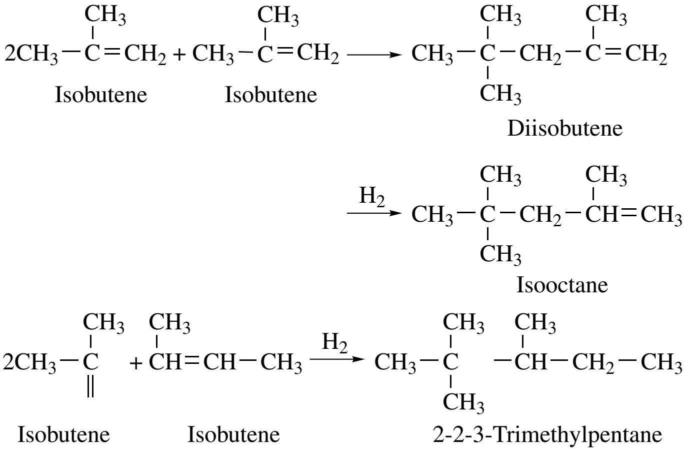
ALKYL. A generic name for any organic group or radical formed from a hydrocarbon by elimination of one atom of hydrogen and so producing a univalent unit. The term is usually restricted to those radicals derived from the aliphatic hydrocarbons, those owing their origin to the aromatic compounds being termed "aryl."

ALKYLATION. Addition of an alkyl group. These reactions are important throughout synthetic organic chemistry; for example, in the production of gasoline with high antiknock ratings for automobiles or for use in aircraft.

The nature of the products of these reactions, as well as the yields, depend upon the catalysts and physical conditions. The reactions in Equation 1 have been written to show two combination reactions of two isobutene molecules, one yielding diisobutene, which reduces to isooctane, and the other yielding a trimethylpentane by a direct reduction reaction. Specifically, the term is applied to various methods, including both thermal and catalytic processes, for bringing about the union of paraffin hydrocarbons with olefins. The process is especially effective in yielding gasoline of high octane number and low boiling range (aviation fuels).



$$\underset{\text{Isobutene}}{2CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} + \underset{\text{Isobutene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} \longrightarrow \underset{\text{Diisobutene}}{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2}$$

$$\xrightarrow{H_2} \underset{\text{Isooctane}}{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}=CH_3}$$

$$\underset{\text{Isobutene}}{2CH_3-\underset{\|}{\overset{CH_3}{\overset{|}{C}}}} + \underset{\text{Isobutene}}{\overset{CH_3}{\overset{|}{CH}}=CH-CH_3} \xrightarrow{H_2} \underset{\text{2-2-3-Trimethylpentane}}{CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3}$$

In the petroleum industry, catalytic cracking units provide the major source of olefinic fuels for alkylation. A feedstock from a catalytic cracking units is typified by a C_3/C_4 charge with an approximate composition of: propane, 12.7%; propylene, 23.6%; isobutane, 25.0%; *n*-butane, 6.9%; isobutylene, 8.8%; 1-butylene, 6.9%; and 2-butylene, 16.1%. The butylenes will produce alkylates with octane numbers approximately three units higher than those from propylene.

One possible arrangement for a hydrofluoric acid alkylation unit is shown schematically in Fig. 1. Feedstocks are pretreated, mainly to remove sulfur compounds. The hydrocarbons and acid are intimately contacted in the reactor to form an emulsion, within which the reaction occurs. The reaction is exothermic and temperature must be controlled by cooling water. After reaction, the emulsion is allowed to separate in a settler, the hydrocarbon phase rising to the top. The acid phase is recycled. Hydrocarbons from the settler pass to a fractionator which produces an overhead stream rich in isobutane. The isobutane is recycled to the reactor. The alkylate is the bottom product of the fractionater (isostripper). If the olefin feed contains propylene and propane, some of the isostripper overhead goes to a depropanizer where propane is separated as an overhead product. A hydrofluoric acid (HF) stripper is required to recover the acid so that it may be recycled to the reactor. HF alkylation is conducted at temperature in the range of 24–38°C (75–100°F).

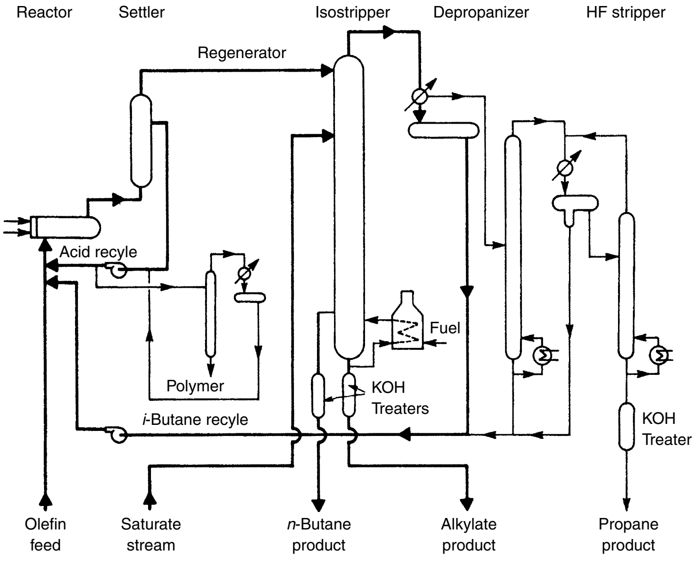


Fig. 1. Hydrofluoric acid alkylation unit. (*UOP Process Division*)

Sulfuric acid alkylation also is used. In addition to the type of acid catalyst used, the processes differ in the way of producing the emulsion, increasing the interfacial surface for the reaction. There also are important differences in the manner in which the heat of reaction is removed. Often, a refrigerated cascade reactor is used. In other designs, a portion of the reactor effluent is vaporized by pressure reduction to provide cooling for the reactor.

ALKYNES. A series of unsaturated hydrocarbons having the general formula C_nH_{2n-2}, and containing a triple bond between two carbon atoms. The simplest compound of this series is acetylene HC:CH. Formerly, the series was named after this compound, namely the *acetylene* series. The latter term remains in popular usage. Particularly, the older names of specific compounds, such as acetylene, allylene CH_2C:CH, and crotonylene CH_3C:CCH_3, persist. These compounds also are sometimes called *acetylenic hydrocarbons*. In the alkyne system of naming, the "yl" termination of the alcohol radical corresponding to the carbon content of the alkyne is changed to "yne." Thus, C_2H_2 (acetylene by the former system) becomes *ethyne*(the "eth" from ethyl (C_2); and C_4H_6 (crotonylene by the former system) becomes *butyne* (the "but" from butyl (C_4)). See also **Organic Chemistry**.

ALLANITE. Allanite is a rather rare monoclinic mineral of somewhat variable but quite complex chemical composition, perhaps represented satisfactorily by the formula $(Ce,Ca,Y)_2(Al,Fe)_3Si_3O_{12}(OH)$. The color of the fresh mineral is black but it is usually brown or yellow with a coating of some alteration product; often the altered crystals have the appearance of small rusty nails. It occurs characteristically in plutonic rocks like granite, syenite or diorite and is found in large masses in pegmatites. Localities in the United States are in New York, New Jersey, Virginia, and Texas. The slender prismatic crystals are sometimes called orthite. Allanite was named for its discoverer, T. Allan. Orthite was so named from the Greek word meaning straight, in reference to the straight prisms, a common habit of this mineral.

ALLELOPATHIC SUBSTANCE. A material contained within a plant that tends to suppress the growth of other plant species. The alkaloids present in several seed-bearing plants are believed to play an allelopathic role. Other suspected allelopathic substances contained in some plants include phenolic acids, flavonoids, terpenoid substances, steroids, and organic cyanides.

ALLOBAR. A form of an element differing in atomic weight from the naturally occurring form, hence a form of element differing in isotopic composition from the naturally occurring form.

ALLOCHROMATIC. With reference to a mineral that, in its purest state, is colorless, but that may have color due to submicroscopic inclusions, or to the presence of a closely related element that has become part of the chemical structure of the mineral. With reference to a crystal that may have photoelectric properties due to microscopic particles occurring in the crystal, either present naturally, or as the result of radiation.

ALLOMERISM. A property of substances that differ in chemical composition but have the same crystalline form.

ALLOTROPES. See **Chemical Elements**.

ALLOYS. Traditionally, an alloy has been defined as a substance having metallic properties and being composed of two or more chemical elements of which at least one is a metal (ASM). Although this still covers the general use of the word, in recent years alloy also has been used in connection with other, non-metallic, materials. Most metals are soluble in one another in their liquid state. Thus alloying procedures usually involve melting. However, alloying by treatment in the solid state without melting can be accomplished in some instances by such methods as powder metallurgy. When molten alloys solidify, they may remain soluble in one another, or may separate into intimate mechanical mixtures of the pure constituent metals. More often, there is partial solubility in the solid state and the structure consists of a mixture of the saturated solid solutions. Another important type of solid phase is the inter-metallic compound, which is characterized by hardness and brittleness and usually has only limited solid solubility with the other phases present. The interactions of two or more elements both in the liquid and solid state are effectively characterized by phase diagrams. Where only two principal materials are involved, *binary alloy* is the term used. Three principal ingredients are referred to as *ternary alloy*. Beyond three components, the material may be referred to as a multi-composition system or alloy.

The decade of the 1980s witnessed the development of hundreds of new alloys, involving not only the traditional metals, but much greater use of the less common chemical elements, such as indium, hafnium, etc. In this encyclopedia, alloys of a chemical element are discussed mainly under that particular element, or in an entry immediately following. Also check alphabetical index.

In addition to the appearance of numerous new alloys, sometimes called superalloys, recent developments in this field include many relatively new processes and methodologies, such as electron beam refining, rapid solidification, single-crystal superalloys, and metallic glasses, among others. Some of these are described in separate articles in this encyclopedia.

Motivation for the development of new alloys is found in nearly all consuming areas, but particular emphasis has been given to the expanding and increasingly demanding requirements of the aircraft and aerospace industries, including much attention directed to the lighter elements (titanium, aluminum, etc.); the needs of the military; the very difficult requirements of jet engine parts; and the electronics industry where much attention has been directed toward the less common metals. Within recent years, metallurgists also have come to appreciate that processing of alloys can be of as much importance as the elements they contain. New processes have been developed during the past decade or so, including rapid solidification, electron beam refining, and many others. Metal alloy research also has been impacted by the rapidly and continuously expanding science and art of making composites, often involving ceramics, graphite, organics, etc. in addition to metals. Knowledge of alloys not only must assist the applications of simply the alloys themselves, but also how the alloys perform in a composite part.

Predicting the Performance of Alloys

It is well known that many important alloy combinations have properties that are not easy to predict, simply on the basis of knowledge of the constituent metals. For example, copper and nickel, both having good electrical conductivity, form solid-solution type alloys having very low conductivity, or high resistivity, making them useful as electrical resistance wires. In some cases very small amounts of an alloying element produce remarkable changes in properties, as in steel containing less than 1% carbon with the balance principally iron. Steels and the age-hardening alloys depend on heat treatment to develop special properties such as great strength and hardness. Other properties which can be developed to a much higher degree in alloys than in pure metals include corrosion-resistance, oxidation-resistance at elevated temperatures, abrasion- or wear-resistance, good bearing characteristics, creep strength at elevated temperatures, and impact toughness. However, solid state physics has been successful in explaining many of these properties of metal and alloys.

There are various types of alloys. Thus, the atoms of one metal may be able to replace the atoms of the other on its lattice sites, forming a substitutional alloy, or solid solution. If the sizes of the atoms, and their preferred structures, are similar, such a system may form a continuous series of solutions; otherwise, the miscibility may be limited. Solid solutions, at certain definite atomic proportions, are capable of undergoing an order-disorder transition into a state where the atoms of one metal are not distributed at random through the lattice sites of the other, but form a superlattice. Again, in certain alloy systems, inter-metallic compounds may occur, with certain highly complicated lattice structures, forming distinct crystal phases. It is also possible for light, small atoms to fit into the interstitial positions in a lattice of a heavy metal, forming an interstitial compound.

In this encyclopedia alloys of chemical elements of alloying importance are discussed under that particular element.

Alloy Phase Diagram Data Programme

Alloy phase diagrams have been known since 1829 when the Swedish scientist Rydberg, who observed the thermal effects that occur during the cooling of binary and ternary alloys from a molten condition. Gibbs many years later published a treatise on the theory of heterogeneous equilibria. The practical importance of phase diagrams awaited the development of the phase diagram for the iron-carbon system, which became central to the metallurgy of steel. See **Iron Metals, Alloys, and Steels**. With the development over the years of scores of binary alloys, considering the number of chemical elements involved, and then followed by ternary and much more complex alloys—with many hundreds of professionals in the metal sciences contributing knowledge—the problems of collecting and of easily locating such information took on formidable proportions. The start of an effective database was the publication of a compilation, by Hansen in 1936, of information gleaned from the literature on 828 binary systems, for which sufficient data were available to construct phase diagrams for 456 binary systems. An English version of the German works, updated to some extent, appeared in 1958. This compilation included 1324 binary systems and 717 binary phase diagrams. A supplementary volume by R.P. Elliott brought the number of binary phase diagrams to 2067 and a later work by F.A. Skunk (1969) included data on 2380 systems. These efforts became key reference works for metallurgists concerned with alloy development and alloy applications. For obvious reasons, information on ternary phase diagrams and other multicomponent systems was far less satisfactory.

To improve this important metallurgical database, the National Bureau of Standards (U.S.) and the American Society for Metals, after many prior deliberations, each signed a memorandum of agreement to proceed with a data programme for alloy phase diagrams, concentrating on binary systems. As early as 1975, T.B. Massalski (Carnegie-Mellon University), then chairman of the programme, observed that a knowledge of phase diagram data is basic for the technological application of metals and alloys; that any programme to provide critically evaluated data would have to be a worldwide enterprise because there is too much work for any institution or organization, or even any country, to accomplish the task alone; that the programme should deal with binary and multicomponent systems; that a computerized bibliographic database should be developed; that computer technology should be used to provide data for the generation of phase diagrams at remote terminals; and that funding for the programme should be sought. As of the late 1980s, many of these objectives had been achieved. Among organizations not previously mentioned, cooperation has been given by the Institute of Metals (U.K.), the U.K. Universities' Science Research Council, the Max-Planck Institut für Metallforschung (Stuttgart), among several other sources, including funding from various interested corporations.

The massive task required that data be sorted into categories by some thirty editors. The first comprehensive publication to be released thus far is from the American Society for Metals (ASM International), entitled "Binary Alloy Phase Diagrams," which contains up-to-date and comprehensive phase diagram information for more than 1850 alloy systems, representing the first major release of critically evaluated phase diagrams since 1969.

Importance of Phase Diagrams

As pointed out by Massalski and Prince (1986), phase diagrams are graphic displays of the thermodynamic relationships of one or more elements at different temperatures and pressures. It has been stated that phase diagrams are to the metallurgist what anatomy is to the medical profession or cartography to the explorer. To explain this analogy, reference is made to a specific phase diagram (Fig. 1). This gold-silicon (Au-Si) phase diagram is a two-dimensional mapping of the phases that form between Au and Si as a function of temperature and of alloy composition. In Fig. 1(a), the alloy composition is defined in terms of the percentage of atoms of Si in the alloy. It will be noted that a dramatic lowering of the freezing point of pure gold (1064.43°C) occurs upon the addition of silicon. Conversely, there is a more regular depression of the freezing point of Si (1414°C) upon the addition of Au.

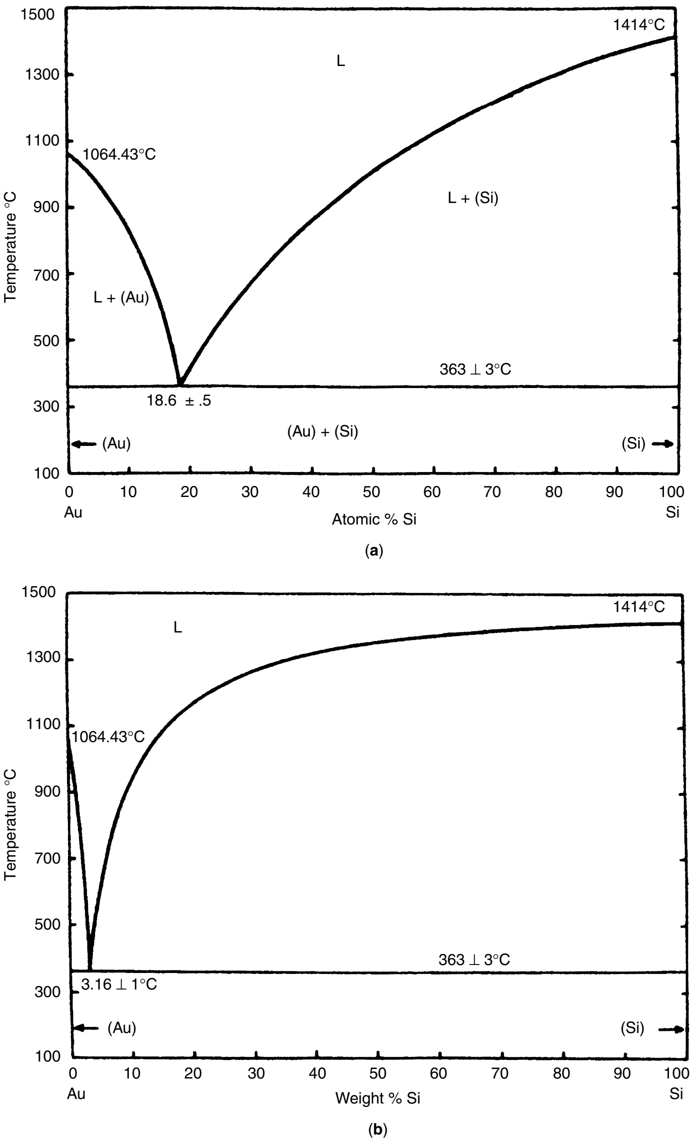


Fig. 1. Representative binary alloy phase diagrams: **(a)** the Au-Si phase diagram with compositions in atomic percent; **(b)** the Au-Si phase diagram with compositions in weight percent. (*ASM News*)

The two upper curves, termed the *liquidus curve*, define the temperatures at which Au-Si alloys begin to solidify. The curves meet at 363°C at an alloy composition containing 18.6 atomic percent Si. At this temperature, all Au-Si alloys, irrespective of composition, complete their solidification by the eutectic separation of a fine mixture of Au and Si from the liquid phase containing 18.5 atomic percent Si. The horizontal line at 363°C is called the *solidus* because below such a line all of the alloys are completely solid.

The effect of presenting the alloy composition in terms of the weight percentage of Si is shown in Fig. 1(b). The liquidus curves drop even more dramatically towards the Au-rich side of the phase diagram and the eutectic liquid at 363°C contains only 3.16 weight percent Si. The movement of the eutectic composition, the lowest-melting alloy composition, from 18.6 percent Si of Fig. 1(a) to 3.15 weight percent Si in Fig. 1(b) simply reflects the great difference in the atomic weights of Au and Si.

Massalski and Prince selected this particular phase diagram because of its simplicity for illustration and because this particular phase diagram is of considerable importance in the semiconductor device industry. Silicon chips are frequently bonded to a heat sink, using a gold alloy or more frequently a Au-Si alloy foil placed between them. Upon heating above 363°C, the Au reacts with Si to form a brazed joint between the silicon chip and the heat sink.

Phase diagrams are condensed presentations of a large amount of information. They provide quantitative information on the phases present under given conditions of alloy composition and temperature and, to the experienced metallurgist, a guide to the distribution of the phases in the microstructure of the alloy. They also dictate what alterations in phase constitution will occur with changing conditions, whether these be alteration of alloy composition, temperature, pressure or atmosphere in equilibrium with the material.

Further, the phases present in an alloy and their morphological distribution within the microstructure, define the mechanical, chemical, electrical, and magnetic properties that may be achievable. Thus, we have the essential link between the engineering properties of an alloy and its phase diagram. Indeed, a distinctive feature of metallurgy as a profession is that it is primarily concerned with the relationship between the constitution and the properties of alloys. Phase diagram data are key elements to understanding, and thereby controlling, the properties of alloys.

Broad Categories of Alloys

Although there are thousands of alloys, with many new alloys appearing each year, there are certain traditional alloys that serve the vast majority of materials needs. The bulk of new alloys, although extremely important, are frequently application-specific. The broad classes are described briefly as follows.

Cast Ferrous Metals.

Gray, Ductile, and High-Alloy Irons

In gray iron, most of the contained carbon is in the form of graphite flakes, dispersed throughout the iron. In ductile iron, the major form of contained carbon is graphite spheres, which are visible as dots on a ground surface. In white iron, practically all contained carbon is combined with iron as iron carbide (cementite), a very hard material. In malleable iron, the carbon is present as graphite nodules. High-alloy irons usually contain an alloy content in excess of 3%.

Malleable Iron

The two main varieties of malleable iron are ferritic and pearlitic, the former more machinable and more ductile; the latter stronger and harder. Carbon in malleable iron ranges between 2.30 and 2.65%. Ranges of other constituents are: manganese, 0.30 to 0.40%; silicon, 1.00 to 1.50%; sulfur, 0.07 to 0.15%; and phosphorus, 0.05 to 0.12%.

Carbon and Low-Alloy Steels

Low-carbon cast steels have a carbon content less than 0.20%; medium-carbon steels, 0.20 to 0.50%; and high-carbon steels have in excess of 0.50% carbon. Ranges of other constituents are: manganese, 0.50 to 1.00%; silicon, 0.25 to 0.80%; sulfur, 0.060% maximum; and phosphorus, 0.050% maximum.

Low-alloy steels have a carbon content generally less than 0.40% and contain small amounts of other elements, depending upon the desired end-properties. Elements added include aluminum, boron, chromium, cobalt, copper, manganese, molybdenum, nickel, silicon, titanium, tungsten, and vanadium.

High-Alloy Steels

When "high-alloy" is used to describe steel castings, it generally means that the castings contain a minimum of 8% nickel and/or chromium. Commonly thought of as stainless steels, nevertheless *cast grades* should be specified by ACI (Alloy Casting Institute) designations and not by the designations that apply to similar *wrought alloys*.

Wrought Ferrous Metals.

Carbon Steels

These steels account for over 90% of all steel production. There are numerous varieties, depending upon carbon content and method of production. In one classification, there are *killed* steels, *semikilled* steels, *rimmed* steels, and *capped* steels. These are described in considerable detail under **Iron Metals, Alloys, and Steels**.

High-Strength Low-Alloy Steels

There are several varieties, with high-yield strength depending mainly on the precipitation of martensitic structures from an austenitic field during quenching. Small additions of alloy elements, such as manganese and copper, are dissolved in a ferritic structure to obtain high strength and corrosion resistance.

Low and Medium-Alloy Steels

The two basic types are (1) *through* hardenable, and (2) *surface* hardenable. Subcategories of surface hardenable alloys include carburizing alloys, flame and induction-hardening alloys, and nitriding alloys.

Stainless Steels

A stainless steel is defined as iron-chromium alloy that contains at least 11.5% chromium. There are three major categories: (1) austenic, (2) ferritic, and (3) martensitic, depending upon the metallurgical structure. There are scores of varieties. Type 302 is the base alloy for austenitic stainless steels. Representative stainless steels in this category provide some insight into why so many varieties are made, and how rather small changes in composition and production can bring about significant differences in the final properties of the various stainless steels. A slightly lower carbon content improves weldability and inhibits carbide formation. An increase in nickel content lowers the work hardening. By increasing both chromium and nickel, better corrosion and scaling resistance is achieved. The addition of sulfur or selenium increases machinability. The addition of silicon increases scaling resistance at high temperature. Small amounts of molybdenum improve resistance to pitting corrosion and temperature strength.

High-Temperature, High-Strength, Iron-Base Alloys

There are two general objectives in making these alloys: (1) they can be strengthened by a martensitic type of transformation, and (2) they will remain austenitic regardless of heat treatment and derive their strength from cold working or precipitation hardening. Again, there are numerous types. Considering the main types, the carbon content may range from 0.05% to 1.10%; manganese, 0.20 to 1.75%; silicon, 0.20 to 0.90%; chromium, 1.00 to 20.75%; nickel, 0 to 44.30%; cobalt, 0 to 19.50%; molybdenum, 0 to 6.00%; vanadium, 0 to 1.9%; tungsten, 0 to 6.35%; copper, 0 to 3.30%; columbium (niobium), 0 to 1.15%; tantalum, 0 to <1%; aluminum, 0 to 1.17%; and titanium, 0 to 3%.

Ultrahigh-Strength Steels

Normally a steel is considered in this category if it has a yield strength of 160,000 psi or more. The first of these steels to be produced was a chromium-molybdenum alloy steel, shortly followed by a stronger chromium-nickel-molybdenum grade.

Free-Machining Steels

Normally, the carbon content is kept under 0.10%, but as much as 0.25% carbon has little deleterious effect on machinability. Aluminum and silicon are held to a minimum (aluminum not used as a de-oxidizer where machinability is extremely important). Lead, sulfur, bismuth, selenium, and tellurium (0.04%) improve machinability when in the proper combination. Sulfur improves machinability by combining with any manganese and oxygen present to form oxysulfides.

Nonferrous Metals.

Aluminum Alloys

These alloys are available as wrought or cast alloys. The principal metals alloyed with aluminum include copper, manganese, silicon, magnesium, and zinc. These alloys are discussed in considerable detail under **Aluminum Alloys**.

Copper Alloys

These alloys are available as wrought or cast alloys. The principal wrought copper alloys are the brasses, leaded brasses, phosphor bronzes, aluminum bronzes, silicon bronzes, beryllium coppers, cupronickels, and nickel silvers. The major cast copper alloys include the red and yellow brasses, manganese, tin, aluminum, and silicon bronzes, beryllium coppers, and nickel silvers. The chemical compositions range widely. For example, a leaded brass will contain 60% copper, 36 to 40% zinc, and lead up to 4%; a beryllium copper is nearly all copper, containing 2.1% beryllium, 0.5% cobalt, or nickel, or in another formulation, 0.65% beryllium, and 2.5% cobalt.

Nickel Alloys

Although nickel is present in varying amounts in stainless steel *commercially* a high-nickel stainless steel is not categorized as a nickel *alloy*, but rather as a stainless steel. Most nickel alloys are proprietary formulations and hence designated by trade names, such as *Duranickel, Monel* (several), *Hastelloy* (several), *Waspaloy, Rene 41, Inco, Inconel* (several), and *Illium* G. The nickel content will range from about 30% to nearly 95%.

Magnesium Alloys

It is the combination of low density and good mechanical strength which provides magnesium alloys with a high strength-to-weight ratio. Again, these generally are proprietary formulations. Aluminum, manganese, thorium, zinc, zirconium, and some of the rare-earth metals are alloyed with magnesium.

Zinc Alloys

Zinc alloys are available as die-casting alloys or wrought alloys. The sprincipal alloys used for die casting contain low percentages of magnesium, from 3.5 to 4.3% aluminum, and carefully controlled amounts of iron, lead, cadmium, and tin.

Titanium Alloys

The titanium-base alloys are considerably stronger than aluminum alloys and superior to most alloy steels in several respects. Several types are available. Alloying metals include aluminum, vanadium, tin, copper, molybdenum, and chromium.

Metallic Glasses. Potentially, metallic glasses and metastable crystalline alloys are the strongest, toughest, and most corrosive resistant, and the most easily magnetizable materials known to materials engineers. Metallic glasses often are quite superior to their crystalline counterparts. This is an important reason why rapid solidification technology has attracted worldwide attention. Several factors are recognized as affecting an alloy's ability to form a metallic glass. These include atomic size ratio, alloy crystallization temperature and melting point, and heat of formation of compounds. In addition to drastic supercooling of a metal alloy, metallic glasses have been made by electro-deposition or by vapor deposition. These non-crystalline metal or alloy compounds are sometimes referred to as *amorphous* alloys.

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ALLYL ALCOHOL AND MONOALLYL DERIVATIVES. The technology of introducing a new functional group to the double bond of allyl alcohol was developed in the mid-1980s. Allyl alcohol is accordingly used as an intermediate compound for synthesizing raw materials such as epichlorohydrin and 1,4-butanediol, and this development is bringing about expansion of the range of uses of allyl alcohol.

Physical Properties

Allyl alcohol is a colorless liquid having a pungent odor; its vapor may cause severe irritation and injury to eyes, nose, throat, and lungs. It is also corrosive. Allyl alcohol is freely miscible with water and miscible with many polar organic solvents and aromatic hydrocarbons, but is not miscible with *n*-hexane. It forms an azeotropic mixture with water and a ternary azeotropic mixture with water and organic solvents. Allyl alcohol has both bacterial and fungicidal effects. Properties of allyl alcohol are shown in Table 1.

Chemical Properties

Addition Reactions. The C=C double bond of allyl alcohol undergoes addition reactions typical of olefinic double bonds.

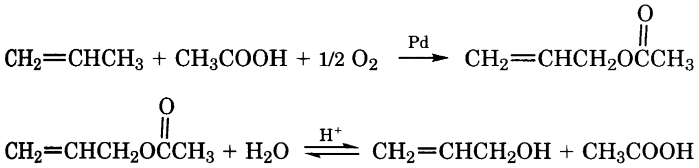
Hydroformylation. Hydroformylation of allyl alcohol is a synthetic route for producing 1,4-butanediol, a raw material for poly(butylene terephthalate), an engineering plastic.

Substitution of Hydroxyl Group. The substitution activity of the hydroxyl group of allyl alcohol is lower than that of the chloride group of allyl chloride and the acetate group of allyl acetate. However, allyl alcohol undergoes substitution reactions under conditions in which saturated alcohols do not react. Reactions proceed in catalytic systems in which a π-allyl complex is considered as an intermediate.

Oxidation. The C=C double bond of allyl alcohol undergoes epoxidation by peroxide, yielding glycidol. This epoxidation reaction is applied in manufacturing glycidol as an intermediate for industrial production of glycerol.

Industrial Manufacturing Processes for Allyl Alcohol

There are four processes for industrial production of allyl alcohol. One is alkaline hydrolysis of allyl chloride. A second process has two steps. The first step is oxidation of propylene to acrolein and the second step is reduction of acrolein to allyl alcohol by a hydrogen transfer reaction, using isopropyl alcohol. At present, neither of these two processes is being used industrially. Another process is isomerization of propylene oxide. Until 1984, all allyl alcohol manufacturers were using this process. Since 1985 Showa Denko K.K. has produced allyl alcohol industrially by a new process which they developed. This process, which was developed partly for the purpose of producing epichlorohydrin via allyl alcohol as the intermediate, has the potential to be the main process for production of allyl alcohol. The reaction scheme is as follows:



$$CH_2{=}CHCH_3 + CH_3COOH + 1/2\ O_2 \xrightarrow{Pd} CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C}CH_3$$

$$CH_2{=}CHCH_2O\overset{\overset{O}{\|}}{C}CH_3 + H_2O \xrightleftharpoons{H^+} CH_2{=}CHCH_2OH + CH_3COOH$$

TABLE 1. PROPERTIES OF ALLYL ALCOHOL

Property	Value
molecular formula	C_3H_6O
molecular weight	58.08
boiling point, °C	96.90
freezing point, °C	−129.00
density, $d^{20}{}_4$	0.8520
refractive index, $n^{20}{}_D$	1.413
viscosity at 20°C, mPa·s(= cP)	1.37
flash point[a] °C	25
solubility in water at 20°C, wt %	infinity

[a] Closed cup.

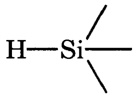
The world's manufacturers of allyl alcohol are ARCO Chemical Company, Showa Denko K.K., Daicel Chemical Industries, and Rhône-Poulenc Chimie; total production is approximately 70,000 tons per year.

Monoallyl Derivatives

In this article, mainly monoallyl compounds are described. Diallyl and triallyl compounds used as monomers are covered elsewhere.

Reactivity of Allyl Compounds

Hydrosilylation. The addition reaction of silane



to the C=C double bond of allyl compounds is applied in the industrial synthesis of silane coupling agents.

π-Allyl Complex Formation. Allyl halide, allyl ester, and other allyl compounds undergo oxidative addition reactions with low atomic valent metal complexes to form π-allyl complexes.

Physical Properties of Derivatives

The physical properties of some important monoallyl compounds are summarized in Table 2.

Allyl Chloride

This derivative, abbreviated AC, is a transparent, mobile, and irritative liquid. It can be easily synthesized from allyl alcohol and hydrogen chloride. However, it is industrially produced by chlorination of propylene at high temperature.

Uses. Allyl chloride is industrially the most important allyl compound among all the allyl compounds. It is used mostly as an intermediate compound for producing epichlorohydrin, which is consumed as a raw material for epoxy resins.

Allyl Esters

Allyl Acetate. Allyl acetate is produced mostly for manufacturing allyl alcohol.

Allyl Methacrylate. At present, allyl methacrylate, AMA, is used mostly as a raw material for silane coupling agents.

Allyl Ethers

The C−H bond of the allyl position easily undergoes radical fission, especially in the case of allyl ethers, reacting with the oxygen in the air to form peroxide compounds.

Therefore, in order to keep allyl ether for a long time, it must be stored in an air-tight container under nitrogen.

Allyl Glycidyl Ether. This ether is used mainly as a raw material for silane coupling agents and epichlorohydrin rubber.

Allyl Amines

Allylamine. This amine can be synthesized by reaction of allyl chloride with ammonia at the comparatively high temperature of 50–100°C, or at lower temperatures using $CuCl_2$ or CuCl as the catalyst.

Dimethylallylamine. Dimethylallylamine is used in the production of insecticides and pesticides.

Safety and Handling

Most allyl compounds are toxic and many are irritants. Those with a low boiling point are lachrymators. Precautions should be taken at all times to ensure safe handling.

Nobuyuki Nagato
Showa Denko K.K.

Additional Reading

Allyl Alcohol, Technical Publication SC: 46-32, Shell Chemical Corp., San Francisco, CA, Nov. 1, 1946.

Schildknecht, C.E.: *Allylic Compounds and Their Polymers,* John Wiley & Sons, Inc., New York, NY, 1973.

Raech, H. Jr.: *Allylic Resins and Monomers,* Reinhold Publishing Corporation, New York, NY, 1965.

ALLYL CHLORIDE. See **Chlorinated Organics**; **Allyl Alcohol and Monoallyl Derivatives**.

ALLYL ESTER RESINS. The allyl radical ($CH_2CH{=}CH_2$) is the basis of the allyl family of resins. Allyl esters are based on monobasic and dibasic acids and are available as low-viscosity monomers and thermoplastic prepolymers. They are used as crosslinking agents for unsaturated polyester resins and in the preparation of reinforced thermoset molding compounds and high-performance transparent articles. All modern thermoset techniques may be used for processing allyl resins.

The most widely used allyls are the monomers and prepolymers of diallyl phthalate and diallyl isophthalate. These are readily converted into thermoset molding compounds and into preimpregnated glass cloths and papers.

Diethyleneglycol-*bis*-(allylcarbonate), marketed as *CR-39*™, is finding increasing use where optical transparency is required. It is the primary material used in the manufacture of *plastic lenses for eyewear* because of its light weight, dimensional stability, abrasion resistance, and dyeability. Other applications for this product include instrument panel covers, camera filters, and myriad glazing uses. In these applications, the solvent and chemical resistance of the material are important.

Other allyl monomers of commercial significance are diallyl fumarate and diallyl maleate. These highly reactive trifunctional monomers contain two types of polymerizable double bonds.

Allyl methacrylate also exhibits dual functionality and finds use as both a crosslinking agent and as a monomer intermediate. Triallyl cyanurate has found use as a crosslinking agent in unsaturated polyester resins.

Most diallyl phthalate compounds are used in critical electrical/electronic applications requiring high reliability under long-term adverse environmental conditions. Compatibility with modern electronic finishing technology, such as vapor phase soldering, is inherent in these materials.

E. J. Sare
PPG Industries Inc.

ALPHA (α). 1. A prefix denoting the position of substituting atom or group in an organic compound. The Greek letters α, β, γ, etc., are usually not identical with the IUPAC numbering system 1, 2, 3, etc., since they

TABLE 2. PROPERTIES OF IMPORTANT ALLYL COMPOUNDS

Property	Allyl chloride	Allyl acetate	Allyl methacrylate	AGE[a]	Allyl amine	DMAA[b]
molecular formula	C_3H_5Cl	$C_5H_8O_2$	$C_7H_{10}O_2$	$C_6H_{10}O_2$	C_3H_7N	$C_5H_{11}N$
molecular weight	76.53	100.12	126.16	114.14	57.10	85.15
boiling point, °C	44.69	104	150	153.9	52.9	64.5
freezing point, °C	−134.5	−96	−60	−100	−88.2	
density, $d^{20}{}_4$	0.9382	0.9276	0.934	0.9698	0.7627	0.72
viscosity at 20°C, mPa · s(= cP)	3.36	0.52	13	1.20		0.44
flash point, °C	−31.7	6	33	57.2	−29	−23

[a] Allyl glycidyl ether.

[b] Dimethylallylamine.

do not start from the same carbon atom. However, α and β are used with naphthalene ring compounds to show the 1 and 2 positions, respectively. α, β, etc., are also used to designate attachment to the side chain of a ring compound.

2. Both a symbol and a term used for relative volatility in distillation.
3. Symbol for optical rotation.
4. A form of radiation consisting of helium nuclei.
5. The major allotropic form of a substance, especially of metals, e.g., α-iron.

ALPHA DECAY. The emission of alpha particles by radioactive nuclei. The name *alpha particle* was applied in the earlier years of radioactivity investigations, before it was fully understood what alpha particles are. It is known now that alpha particles are the same as helium nuclei. When a radioactive nucleus emits an alpha particle, its atomic number decreases by $Z = 2$ and its mass number by $A = 4$. The process is a spontaneous nuclear reaction, and the radionuclide that undergoes the emission is known as an *alpha emitter*.

The entire energy released by the transition is carried away by the product nuclei. Therefore, a spectrum of alpha-particle numbers as a function of energy shows a series of distinct peaks, each corresponding to a single alpha-particle transition. To conserve both energy and momentum, the energy must be shared by the two product nuclei, with the daughter nucleus ($^{A-4}Z - 2$) recoiling away from the direction of emission of the alpha particle. If E_X and M_X are, respectively, the kinetic energy and mass of the alpha particle and E_R and M_R the kinetic energy and mass of the recoiling product nucleus, the transition energy is $Q = E_\alpha + E_R$; and the kinetic energy of the emitted alpha particle is $E_\alpha = [M_R(M_\alpha + M_R)]Q$.

Almost all radioactive nuclides that emit alpha particles are in the upper end of the periodic table, with atomic numbers greater than 82 (lead), but a few alpha-particle emitting nuclides are scattered through lower atomic numbers. The reason why alpha-particle emitters are limited to nuclides with larger mass numbers is that generally only in this region is alpha-particle emission energetically possible. Most radioactive nuclides with smaller mass numbers emit beta-particle radiation.

See **Particles (Subatomic)**; and **Radioactivity**.

ALPHA PARTICLE. A helium nucleus emitted spontaneously from radioactive elements both natural and, man-made. Its energy is in the range of 4–8 MeV and is dissipated in a very short path, i.e., in a few centimeters of air or less than 0.005 mm of aluminum. It has the same mass (4) and positive charge (2) as the helium nucleus. Accelerated in a cyclotron alpha-particles can be used to bombard the nuclei of other elements.

See also **Beta Decay**; **Helium**; and **Radioactivity**.

ALTMAN, SIDNEY (1939–). Awarded the Nobel prize in Chemistry in 1989 jointly with Thomas R. Cech for the discovery that RNA acts as a biological catalyst as well as a carrier of genetic information. He received his Doctorate in 1967 from the University of Colorado.

ALUM. A series (*alums*) of usually isomorphous crystalline (most commonly octahedral) compounds in which sulfate is usually the negative ion. Alums have the general formula $M^{I}\,M^{III}\,(AX_4)\cdot 12H_2O$. The first is potassium or a higher alkali metal (sodium alums are rare) or thallium(I) or ammonium (or a substituted ammonium ion) and the second is a tripositive ion of relatively small ionic radius (0.5–0.7Å). The tripositive ions of larger ionic radius such as the Lanthanides form double sulfates, but not alums. The tripositive ions in alums, in roughly the order of number of known compounds, are aluminum, chromium, iron, manganese, vanadium, titanium, cobalt, gallium, rhodium, iridium, and indium.

The term *alum*, itself, refers to potassium alum, potassium aluminum sulfate, $KA1(SO_4)_2 \cdot 12H_2O$. Other common alums are ferric ammonium alum, $NH_4\ Fe(SO_2)_2 \cdot 12H_2O$, and sodium chrome alum, $NaCr(SO_4)_2 12H_2O$.

ALUMINA. See **Adsorption**; and **Bauxite**.

ALUMINUM. [CAS: 7429-90-5]. Chemical element symbol Al, at. no. 13, at. wt. 26.98, periodic table group 13, mp 660 ± 1°C, bp 2452 ± 15°C, sp gr 2.699. In Canada and several other English-speaking nations, the spelling of the element is *aluminium*. The element is a silver-white metal, with bluish tinge, capable of taking a high polish. Commercial aluminum has a purity of 99% (minimum), is ductile and malleable, possesses good weldability, and has excellent corrosion resistance to many chemicals and most common substances, particularly foods. The electrical conductivity of aluminum (on a volume basis) is exceeded only by silver, copper, and gold. First ionization potential, 5.984 eV; second, 18.823 eV; third, 28.44 eV. Oxidation potentials, $Al \longrightarrow Al^{3+} + 3e^-$, V; $Al + 4OH^- \longrightarrow AlO_2^- + 2H_2O + 3e^-$, 2.35 V. Other important physical properties of aluminum are given under **Chemical Elements**.

Aluminum occurs abundantly in all ordinary rocks, except limestone and sandstone; is third in abundance of the elements in the earth's crust (8.1% of the solid crust), exceeded only by oxygen and silicon, with which two elements aluminum is generally found combined in nature; present in igneous rocks and clays as aluminosilicates; in the mineral cryolite in Greenland as sodium aluminum fluoride Na_3AlF_6; in the minerals corundum and emery, the gems ruby and sapphire, as aluminum oxide Al_2O_3; in the mineral bauxite in southern France, Hungary, Yugoslavia, Greece, the Guianas of South America, Arkansas, Georgia, and Alabama of the United States, Italy, Russia, New Zealand, Australia, Brazil, Venezuela, and Indonesia as hydrated oxide $Al_2O(OH)_4$; in the mineral alunite or alum stone in Utah as aluminum potassium sulfate $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 4Al(OH)_3$. See also **Bauxite**; and **Cryolite**.

Uses

Because of its corrosion resistance and relatively low cost, aluminum is used widely for food-processing equipment, food containers, food-packaging foils, and numerous vessels for the processing of chemicals. Because of the presence of aluminum in soils and rocks, there are natural traces of the element in nearly all foods. The processing of foods in copper vessels will cause destruction of vitamins, whereas aluminum does not accelerate the degradation of vitamins. Aluminum foil has been used to cover severe burns as a means to enhance healing. Because of its good electrical conductivity (exceeded only by gold, silver and copper), aluminum is used as an electrical conductor, particularly for high-voltage transmission lines. For the same conductance, the weight of aluminum required is about one-half that of annealed copper. The greater diameter of aluminum conductors also reduces corona loss. But, because aluminum has about 1.4× the linear temperature coefficient of expansion as compared with annealed copper, the changes in sag of the cable are greater with temperature changes. For long spans requiring high strength, the center strand may be a steel cable, or supporting steel cables may be used. Aluminum is used for bus bars because of its large heat-dissipating surface available for a given conductance.

Aluminum alloys readily with copper, manganese, magnesium, silicon, and zinc. Many aluminum alloys are commercially available. See also **Aluminum Alloys and Engineered Materials**.

Because aluminum, particularly in alloys, combines strength with light weight, it has been a favorite construction material for transportation equipment, such as airplanes, the early dirigibles, and parts of rail cars. With the emphasis on fuel economy during the past decade or two, the automotive industry has become a major user of aluminum alloys. For example, important developments include cast-aluminum engine blocks with metallurgically bonded-in-place cylinder liners, cast-spun wheels, aluminum space frames, and auto radiators. The first mass production of aluminum radiators occurred in the 1980s (Ford Motor Co.) and it is predicted that nearly all Ford vehicles will feature aluminum radiators by the mid-1990s. Of course, other auto firms worldwide are also actively pursuing the metal because of its light weight and other attractive properties.

The applications of aluminum are growing larger and more varied with the introduction of advanced materials engineering techniques, including sandwich-type construction, laminates, aluminum powder metallurgy, and composite technology.

Discovery and Early Production

Although aluminum was predicted by Lavoisier (France) as early as 1782, when he was investigating the properties of aluminum oxide (alumina), the metal was not isolated until 1825 by H.C. Oersted (Denmark). Oersted obtained an impure aluminum metal by heating potassium amalgam with anhydrous aluminum chloride, followed by distilling off the mercury. Using similar methods, Woehler (Germany) produced an aluminum powder in 1827. In 1854, Deville (France) and Bunsen (Germany) separately but concurrently found that aluminum could be isolated by using sodium instead of potassium in the amalgam of Oersted and Woehler. Deville exhibited his product at the Paris Exposition of 1855, after which Napoleon III commissioned Deville to improve the process and lower the cost. Because of improved processing techniques, the price declined from $115 to $17 per pound ($254 to $38 per kilogram) by 1859, with numerous plants throughout France. The price was further reduced to $8 per pound ($17.60 per kilogram) by 1885. The first breakthrough for production of aluminum on a large scale and at a much lower cost occurred as the result of experimentation by Hall (Oberlin, Ohio) who found that metallic aluminum could be produced by dissolving Al_2O_3 (alumina) in molten $3NaF{\cdot}AlF_3$ (cryolite) at a temperature of above 960°C and then passing an electric current through the bath. Heroult (France) independently discovered the same process.

Contemporary Production Methods

For many years the electrolytic process has dominated. The major difference found in aluminum production plants relate to the design of the electrolytic cells. Basically, the cells are large carbon-lined steel boxes. The carbon lining serves as the cathode. Separate anodes are immersed in the bath. The electric circuit is completed by passage of current through the bath. Thus, the alumina is decomposed into aluminum and oxygen by action of the electric current. The molten aluminum collects at the bottom of the cell from which it is siphoned off periodically. The released oxygen combines with carbon at the electrodes to form CO_2. The bath is replenished with alumina intermittently. The carbon anodes must be replaced periodically. Additional cryolite also is required to make up for volatilization losses. The several reactions which occur during electrolysis still are not fully understood.

Energy requirements for aluminum production in modern plants approximate 6 to 8 kilowatt-hours per pound (13.2 to 17.6 kilowatt-hours per kilogram). Per weight unit of aluminum produced, 0.4 to 0.6 weight units of carbon, 1.9 weight units of alumina, and 0.1 weight unit of cryolite are required. One form of electrolytic cell is shown in Fig. 1.

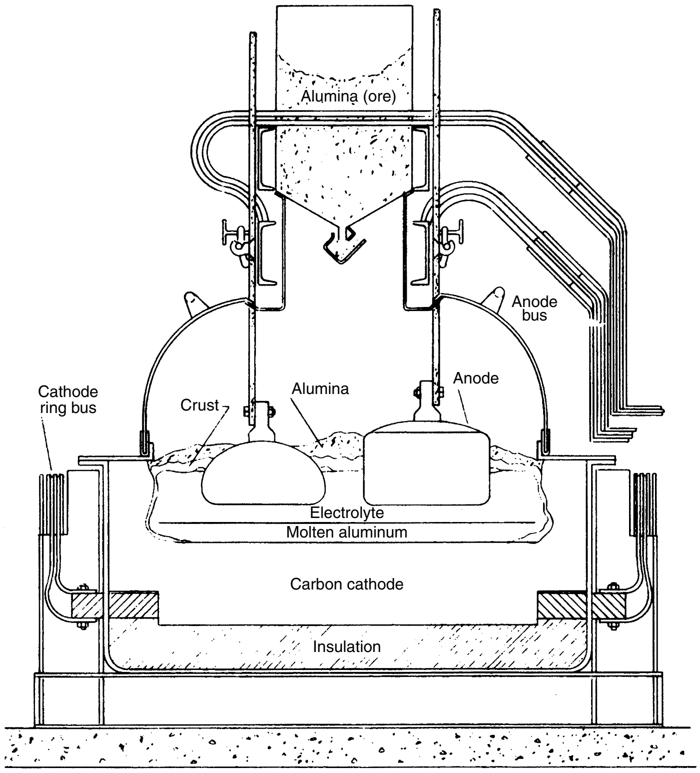


Fig. 1. Aluminum electrolytic reduction cell of the pre-bake type. The anodes are constructed of separate blocks of carbon which have been pre-baked. There is a lead to the main bus bar from each block. (*Reynolds Metals Company*)

An estimate (1987) showed that the aluminum industry accounts for nearly 1.5% of the annual world energy consumption. Because of the need to conserve energy and concurrently to alleviate (even to a small extent) the disposal of solid waste materials, a program was initiated in some industrial nations to collect and recycle the aluminum cans used mainly by the carbonated beverage industry. The program has proved to be more successful than originally predicted. As of 1990, over one-half of the aluminum beverage cans are recycled in the United States. See Figs. 2 and 3. Efforts also have been made to reduce the amount of aluminum needed for each beverage can. The thickness of the aluminum can body has been reduced from an average weight of 21 grams/can in 1972 to approximately 15 grams/can in 1992. Can manufacturers have developed new designs that retain strength while reducing the amount of metal needed. In one innovation, the top of the can was "necked in"—first one, then two, three, and four times. Each successive necking down of the end lowered the weight of the can. By 1990, the average weight/can had been reduced by at least 26%.

Fig. 2. Recycling of aluminum beverage cans and other scrap saves nearly 95% of the energy required when producing the virgin metal from ore. Approximately 50% of the metal processed in 1990 was recycled from scrap. (*Reynolds Aluminum Recycling Company*)

Because of production process improvements, the cost of aluminum has been reduced by many fold over the past century. The demographics of aluminum production have changed markedly in recent years. Since 1982, the virgin metal producers in the United States have closed down or abandoned seven of the older, less-efficient, and higher-cost reduction plants. American producers have gone to other countries to build new modern plants using the most recently developed technology for large electrolytic cells. New generation electrolytic cells operate at very high current densities (180,000–275,000 amperes). These cells will produce four times the output of many existing cells while using 25% less energy.

The principal aluminum-producing areas of the world, in addition to the United States and Europe, are Canada, Venezuela, Brazil, Norway, Australia, and the Republic of the Congo. In the United States the remaining plants are located in the states of Washington, Oregon, and New York, along the Mississippi, and where water power generation is still available at somewhat reduced cost.

In 1960, 90% of world capacity was held by private enterprises. That percentage had dropped to 60% in 1985. The trend is to greater governmental participation in Latin America. Africa, the Mideast, and Asia. Fifty percent of Western World capacity is government sponsored, primarily in Europe and Latin America. Six corporate groups account for 50% of aluminum production. These are Alcan, Alcoa, Reynolds, Kaiser, Pechiney, and Alusuisse. They possess 40% of the bauxite capacity for

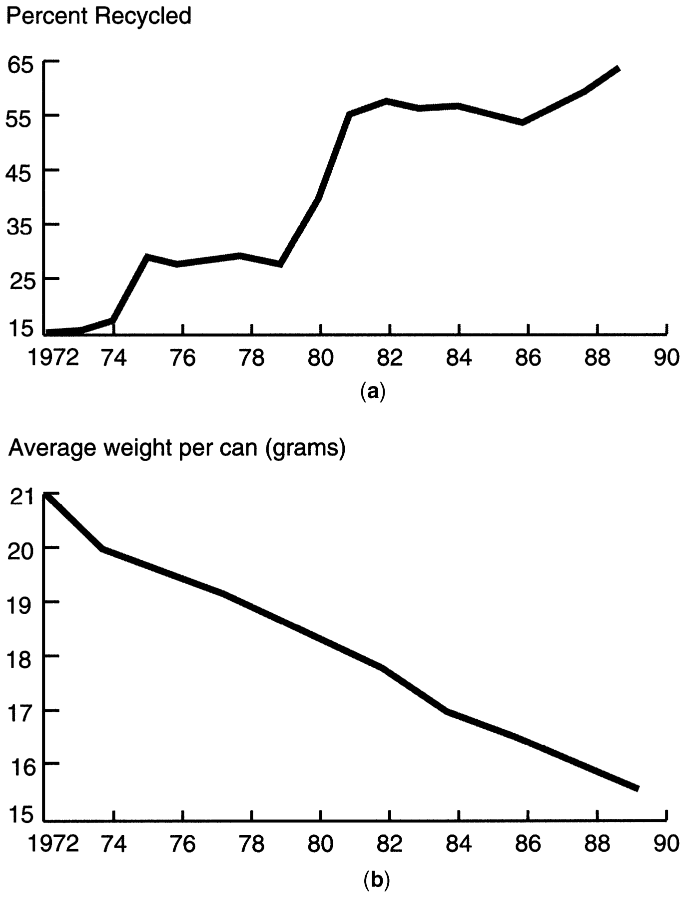


Fig. 3. Steps to conserve aluminum and the electrical power to produce it: **(a)** Percent of aluminum cans recycled (1972–1990); **(b)** average weight of beverage can (grams) (1972–1990). (*Source: Aluminum Association*, Washington, DC)

alumina and aluminum. All are integrated from mine to ultimate consumer. Australia is the world's largest producer of bauxite.[1]

By 1995, Australia will probably be one of the world's three largest aluminum producers. At present, it supplies one-third of the world's bauxite. New smelter construction underway is expected to boost the world production by two million tons (1.8 million metric tons). New Zealand also has a good potential. Australia has coal reserves estimated at 1500 years.

It is also projected that Venezuela, because of its abundance of hydropower, will become a major aluminum producer. During the past decade, Brazil has attracted considerable interest because of its vast reserves of good quality bauxite and hydropower. The Tucurui hydroelectric power facility will double its output by 1995.

The People's Republic of China is modernizing with the help and technology of foreign companies to bring its production to over 500,000 metric tons.

Most of the increased capacity for virgin aluminum production for the past two and a half decades has occurred outside the continental United States. The annual growth rate for the aluminum industry during this period is estimated at about 1.6%. The projected U.S. growth rate is about 1% per year, as contrasted with $2\frac{1}{4}$% worldwide. U.S. consumption is about 50 pounds (22.5 kg) per person per year. World consumption has doubled about every 20 years. The developed nations (North America, Western Europe, Japan-Oceania) account for two-thirds of world consumption of aluminum (1991).

Thermal Reduction Process

Because of the large electric power requirements of the electrolytic process, an effort has been underway for several years to cut production costs. The thermal process, including the use of electric arc furnaces, make it possible to achieve a greater concentration of electric energy in the refining process. Commercial electric furnace processes are fed with bauxite and clays (kaolin or kyanite or partially refined bauxite mixed with carbon or charcoal in briquette form). An electric dc or ac arc is used. To date, this process has been practical only for the production of impure aluminum alloys, ranging in content from 65–70% aluminum, 25–30% silicon, and 1% or more of iron. Other impurities may include titanium and the carbides and nitrides of aluminum and iron. This impure product may be refined to yield pure aluminum by means of a subsequent distillation process in which the electric-furnace product is dissolved at high temperatures in zinc, magnesium, or mercury baths and then distilled. Aluminum with a purity of 99.99 + % may be produced in this manner.

A gas-reaction purification process also has attracted attention over the years. This is based on aluminum trichloride gas reacting with molten aluminum at about 1000°C to produce aluminum monochloride gas. Aluminum fluoride gas may be substituted for the aluminum monochloride gas in the process. Raw materials for the process may be scrap aluminum, aluminum from thermal-reduction processes, aluminum carbide, or aluminum nitride. As of the beginning of 1987, none of these other processes are fully commercial.

For the production of superpurity aluminum on a large scale, the Hoopes cell is used. This cell involves three layers of material. Impure (99.35 to 99.9% aluminum) metal from conventional electrolytic cells is alloyed with 33% copper (eutectic composition) which serves as the anode of the cell. A middle, fused-salt layer consists of 60% barium chloride and 40% $AlF_3 1.5NaF$ (chiolite), mp 720°C. This layer floats above the aluminum-copper alloy. The top layer consists of superpurity aluminum (99.995%). The final product usually is cast in graphite equipment because iron and other container metals readily dissolve in aluminum. For extreme-purity aluminum, zone refining is used. This process is similar to that used for the production of semiconductor chemicals and yields a product that is 99.9996% aluminum and is available in commercial quantities.

Continuing Research and Development

The industry continues to research improvements in the present production cells. Special attention is being focused on developing inert anodes and cathodes. Ferrites may find use as inert anodes, while titanium diboride may become the optimum material for cathodes. Before commercial use of inert electrodes can be achieved, cell sidewall materials must be developed which will withstand extremely reactive conditions and further improvements (i.e., less solubility of the anode and cathode materials are required). Over the past 15 years, American and Canadian aluminum producers have channeled nearly $1.5 billion into manufacturing technology research, the modernization and computerization of plant facilities, and new and better applications for the metal. Some of the results achieved thus far include:

- Energy efficiency—improved by almost 20%.
- New smelters with large, more efficient electrolytic cells.
- Recycling processes for all types of aluminum scrap, including aluminum beverage cans.
- Electromagnetic casting (EMC) for aluminum ingots in which an electromagnetic force field acts as the mold, thus producing smooth surfaces. In many cases, this eliminates wasteful scalping.
- Fluxing and degassing methods, combined with filtration, to give highest quality aircraft and other critical alloys.
- Continuous casting of filtered molten metal into giant coils (50,000 lb; 22,680 kg) of 0.250-inch (~6.4 mm) strip. This eliminates all hot rolling and intermediate annealing for rolling thin sheet products, such as foil, container stock, siding, etc.
- Aluminum particle rolling directly into continuous strip. Molten metal is sprayed into particles about the size of rice in a controlled environment, then brought to a desired rolling temperature and continuously rolled into "instant" coiled sheet This process can handle alloys which normally cannot be cast in ingot form.

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[1] Firms participating in the development of Australian production capacity include Alcan, Alcoa, Kaiser, Comalco, Alumax, Reynolds, Pechiney and several Japanese companies.

- Computerized-automated cold rolling mills capable of 8000 ft (2438 m) per minute speeds. Multistand cold mills eliminate coil changes and wasted time. See Fig. 4.
- Foil rolling at speeds up to 8000 ft (2438 m) per minute with automatic gauge and shape control.
- Aluminum cans have captured over 90% of the beverage industry in the United States. The intent now is to capture a major share of the 30 billion cans food packaging market. (This will be challenged by the increasing use of plastics.)
- Increased use of aluminum in automotive vehicles. Approximately 200 pounds (90 kg) of aluminum per U.S.-built vehicle (i.e., wheels, engine blocks, bumpers, heat exchangers, and other parts).
- New alloys, such as aluminum-lithium alloys for aircraft applications that will permit 7 to 10% weight reduction per aircraft.
- Aluminum powder metallurgy continues to receive high research and development priority. A major objective is to produce final aluminum parts by direct pressing of rapidly solidified aluminum particles. The process handles high-strength aluminum alloy materials.
- Aluminum composites aim at combining high-strength aluminum alloys with alumina ceramic fibers and filaments to provide even higher-strength structural materials.
- Superplastic—high-strength aluminum alloys which can be plastically shaped into difficult designed parts used on cars and aircraft.
- Rheocasting technology for producing stronger castings by combining casting and forging of molten aluminum alloys in one step.
- Ultrasonic welding, used increasingly in the aerospace, automotive, electrical, and electronics industries. The process requires simpler surface preparation and less energy and allows welding of thinner sheets to thicker structural members.
- Inertia (friction) welding in the solid state, which is useful for joining dissimilar metals, i.e., aluminum to steel and stainless steel. At least one of the pieces to be welded must be circular and capable of being rotated at high velocities before being brought into contact with pressure to the second member.
- Vacuum brazing for producing heat exchangers.
- Aluminum as energy (fuel) source. The high energy content of aluminum has made it a logical choice as a sold fuel for boosting vehicles, such as the space shuttle, into orbit.
- Aluminum—air battery. A second potential application of this available energy is based on electrochemical oxidation of aluminum in air to produce electricity. In an aluminum—air battery, for example, thin coils of aluminum strip may be used as the fuel. No electric battery recharging would be required since the aluminum is consumed to generate the electricity directly. This fuel would not give off fumes or pollute and could be stored in solid form indefinitely. If this concept materializes into commercial viability, it will provide the energy needed for electric vehicles.

Some of the foregoing topics are described in more detail in the following article on **Aluminum Alloys and Engineered Materials**.

Aluminum and Space

The year 1986 marked the hundredth anniversary of the Hall-Heroult electrolytic process for producing aluminum economically. Jules Verne, the 19th century fiction writer, foretold the use of aluminum for space travel while it was still a mystery metal. Aluminum is the key metal in the aerospace industry. The Wright brothers recognized its value on their first flight in 1903 by using aluminum to build part of their engine. In military and commercial aircraft, aluminum became the metal of construction as early as 1930 for the U.S. Army P-12 and the Navy F-48, as well as an aluminum dirigible ZNC-2. World War II “light metals war” planes (i.e., B-17, B-25, B-29, etc.) became the forerunners of present aircraft. The U.S. Army Ballistic Missile Agency launched a program in 1950 for surface-to-surface missiles—the Redstone and Jupiter rocket programs. These programs prepared the way for NASA to launch unmanned satellites and to put men on the moon. Aluminum was the metal used for the rockets, the space modules, the moon rover (land vehicle), and most equipment associated with the programs. Today aluminum is used in the solid fuel booster rockets (some containing 0.5 mil lb-0.23 mil kg-of aluminum powder), in the space shuttles and planned space station. Some commercial airliners (jumbo jets 747 and DC-10) contain more than 300,000 lb (~136,000 kg) of aluminum each.

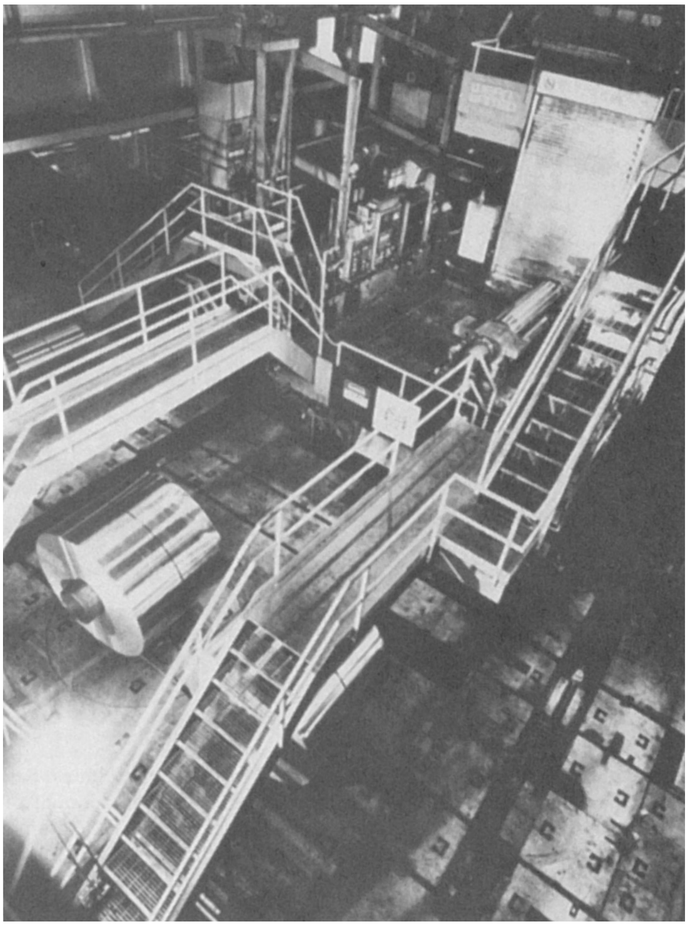

Fig. 4. High-speed, computer-controlled cold rolling mill can roll coils up to 40,000 pounds (18,150 kg), at speeds up to 5500 feet (1675 m) per minute. The system is equipped with automatic hydraulic gage control and shape control systems. (*Reynolds Metals Company*)

Aluminum Chemistry and Chemicals

The CAS registry lists 5037 aluminum-containing compounds exclusive of alloys and intermetallics.

Since aluminum has only three electrons in its valence shell, it tends to be an electron acceptor. Its strong tendency to form an octet is shown by the tetrahedral aluminum compounds involving sp^3 hybridization. Aluminum halides include the trifluoride, an ionic crystalline solid, the trichloride and tribromide both of which are dimeric in the vapor and in nonpolar solvents, having the halogen atoms arranged in tetrahedra about each aluminum atom, giving a bridge structure; and the triiodide. They combine readily with many other molecules, especially organic molecules having donor groups, and aluminum chloride is an active catalyst. Certain of the hydrates have a saltlike nature; thus $AlCl_3 \cdot 6H_2O$ acts as a salt, even though Al_2Cl_6 is covalent.

Common water-soluble salts include the sulfate, selenate, nitrate, and perchlorate, all of which are hydrolyzed in aqueous solution. Double salts are formed readily by the sulfate and by the chloride.

There are many fluorocomplexes of aluminum. The general formula for the fluoroaluminates is $M^1_x\,[Al_yF_{x+3y}]$, based upon AlF_6 octohedra, which may share corners to give other ratios of Al:F than 1:6. Chloroaluminates of the type $M^1[AlCl_4]$ are obtainable from fused melts. Aluminum ions form chloro-, bromo-, and iodo-complexes containing tetrahedral $[AlX_4]^-$ ions. However, in sodium aluminum fluoride $NaAlF_4$, the aluminum atoms are in the centers of octohedra of fluorine atoms in which the fluorine atoms are shared with neighboring aluminum atoms.

Aluminum hydroxide is about equally basic and acidic, the pK_b being about 12 and the pK_a being 12.6. Sodium aluminate seems to ionize as a uni-univalent electrolyte: $NaAl(OH)_4(H_2O)_2 \rightleftharpoons Na^+ + [Al(OH)_4(H_2O)_2]^-$. The high viscosity of sodium aluminate solutions is explained by hydrogen bonding between these hydrated ions, and between them and water molecules. By reaction of aluminum and its chloride or bromide at high temperature, there is evidence of the existence of monovalent aluminum. Here the aluminum atom is apparently in the sp state, with an electron pair on the side away from the chlorine atom, whereby the single pairs on the two chlorine atoms are shared to form two weak π bonds.

Aluminum forms a polymeric solid hydride, $(AlH_3)_x$, unstable above 100°C, extremely reactive, e.g., giving hydrogen explosively with H_2O and igniting explosively in air. From it are derived the tetrahydroaluminates, containing the ion $AlH_4{}^-$, which are important, powerful but selective reducing agents, e.g., reducing chlorophosphines R_2PCl to phosphines R_2PH; reactive alkyl halides and sulfonates to hydrocarbons, epoxides, and carboxylic acids; aldehydes and ketones to alcohols; nitrites, nitro compounds and N,N-dialkyl amides to amines. The salt most commonly used is lithium (tetra)hydroaluminate ("lithium aluminum hydride").

Aluminum compounds are generally made starting with bauxite, which is reactive with acids and with bases. With acids, e.g., H_2SO_4, any iron contained in the bauxite is dissolved along with the aluminum and silicon is left in the residue, whereas with bases, e.g., NaOH, any silicon is dissolved and iron left in the residue.

Acetate: Aluminum acetate $Al(C_2H_3O_2)_3$, white crystals, soluble, by reaction of aluminum hydroxide and acetic acid and then crystallizing. Used (1) as a mordant in dyeing and printing textiles, (2) in the manufacture of lakes, (3) for fireproofing fabrics, (4) for waterproofing cloth.

Aluminates: Sodium aluminate $NaAlO_2$, white solid, soluble, (1) by reaction of aluminum hydroxide and NaOH solution, (2) by fusion of aluminum oxide and sodium carbonate; the solution of sodium aluminate is reactive with CO_2 to form aluminum hydroxide. Used as a mordant in the textile industry, in the manufacture of artificial zeolites, and in the hardening of building stones. See silicates below and calcium aluminates.

Alundum: See oxide (below).

Carbide: Aluminum carbide Al_4C_3, yellowish-green solid, by reaction of aluminum oxide and carbon in the electric furnace, reacts with H_2O to yield methane gas and aluminum hydroxide.

Chlorides: Aluminum chloride $AlCl_3 \cdot 6H_2O$, white crystals, soluble, by reaction of aluminum hydroxide and HCl, and then crystallizing; anhydrous aluminum chloride $AlCl_3$, white powder, fumes in air, formed by reaction of dry aluminum oxide plus carbon heated with chlorine in a furnace, used as a reagent in petroleum refining and other organic reactions.

Fluoride: Aluminum fluoride AlF_3, white solid, soluble, by reaction of aluminum hydroxide plus hydrofluoric acid and then crystallizing $2AlF_3 \cdot 7H_2O$, used in glass and porcelain ware.

Hydroxide: Aluminum hydroxide $Al(OH)_3$, white gelatinous precipitate, by reaction of soluble aluminum salt solution and an alkali hydroxide, carbonate or sulfide (sodium aluminate is formed with excess NaOH but no reaction with excess NH_4OH), upon heating aluminum hydroxide the residue formed is aluminum oxide. Used as intermediate substance in transforming bauxite into pure aluminum oxide.

Nitrate: Aluminum nitrate $Al(NO_3)_3$, white crystals, soluble, by reaction of aluminum hydroxide and HNO_3, and then crystallizing.

Oleate: Aluminum oleate $Al(C_{18}H_{33}O_2)_3$, yellowish-white powder, by reaction of aluminum hydroxide, suspended in hot H_2O, shaken with oleic acid, and then drying, the product is used (1) as a thickener for lubricating oils, (2) as a drier for paints and varnishes, (3) in waterproofing textiles, paper, leather.

Oxide: Aluminum oxide, alumina Al_2O_3, white solid, insoluble, melting point 2020°C, formed by heating aluminum hydroxide to decomposition; when bauxite is fused in the electric furnace and then cooled, there results a very hard glass ("alundum"), used as an abrasive (hardness 9 Mohs scale) and heat refractory material. Aluminum oxide is the only oxide that reacts both in H_2O medium and at fusion temperature, to form salts with both acids and alkalis.

Palmitate: Aluminum palmitate $Al(C_{16}H_{31}O_3)_3$, yellowish-white powder, by reaction of aluminum hydroxide, suspended in hot H_2O, shaken with palmitic acid, and then drying, the product is used (1) as a thickener for lubricating oils, (2) as a drier for paints and varnishes, (3) in waterproofing textiles, paper, leather, (4) as a gloss for paper.

Silicates: Many complex aluminosilicates or silicoaluminates are found in nature. Of these, clay in more or less pure form, pure clay, kaolinite, kaolin, china clay $H_4Si_2AlO_2O_9$ or $Al_2O_3.2SiO_2.2H_2O$ is of great importance. Clay is formed by the weathering of igneous rocks, and is used in the manufacture of bricks, pottery, procelain, and Portland cement.

Stearate: Aluminum stearate $Al(C_{18}H_{35}O_2)_3$, yellowish-white powder, by reaction of aluminum hydroxide suspended in hot H_2O, shaken with stearic acid, and then drying the product, used (1) as a thickener for lubricating oils, (2) as a drier for paints and varnishes, (3) in waterproofing textiles, paper, leather, (4) as a gloss for paper.

Sulfate: Aluminum sulfate $Al_2(SO_4)_3$, white solid, soluble, by reaction of aluminum hydroxide and H_2SO_4, and then crystallizing, used (1) as a clarifying agent in water purification, (2) in baking powders, (3) as a mordant in dyeing, (4) in sizing paper, (5) as a precipitating agent in sewage disposal; aluminum potassium sulfate, see **Alum**; and **Alunite**.

Sulfide: Aluminum sulfide Al_2S_3, white to grayish-black solid, reactive with water to form aluminum hydroxide and H_2S, formed by heating aluminum powder and sulfur to a high temperature.

Aluminum in solution of its salts is detected by the reaction (1) with ammonium salt of aurin tricarboxylic acid ("aluminon"), which yields a red precipitate persisting in NH_4OH solution, (2) with alizarin red S, which yields a bright red precipitate persisting in acetic acid solution.

Organoaluminum Compounds: By the action of alpha olefins on AlH_3, the trialkyls of aluminum can be prepared:

$$AlH_3 + 3CH_2 = CHR \xrightarrow{120^\circ} (CH_2CH_2R)Al$$

In the presence of ethers, magnesium-alloy alloys react with alkyl halides to yield trialkyls, R_3AlOEt_2. The trimethyl aluminum compound is a dimer, mp 15°C. Triethyl aluminum is a liquid. The alkyls react readily with H_2O:

$$Et_3Al + 3H_2O \longrightarrow Al(OH)_3 + 3EtH$$

When aluminum is reacted with diphenyl mercury $(C_6H_5)_2Hg$, triphenylaluminum $(C_6H_5)_3Al$ is yielded. The aluminum organometallic alkyls and aryls act as Lewis acids to form compounds with electron-donating substances. The resulting compounds are the organometallic basis for producing polymers of the Al-N type.

Zeolite Structures: These are crystalline, microporous solids that contain cavities and channels of molecular dimensions (3 Å to 10Å) and sometimes are called molecular sieves. Zeolites are used principally in catalysis, separation, purification, and ion exchange. The fundamental building block of a zeolite is a tetrahedron of four oxygen atoms surrounding a central silicon atom (i.e., $(SiO_4)^{4-}$) . From the fundamental unit, numerous combinations of secondary building units (polygons) can be formed. The corners of these polyhedra may be Si or Al atoms.[2]

Different combinations of the same secondary building unit may yield numerous distinctive zeolites. As pointed out by D.E.W. Vaughan, few fields of chemistry offer such chemical and structural diversity. Although only about sixty structures are known, tens of thousands of theoretical structures are possible. The science of synthesizing zeolites, which achieves much more diversity than is the case with natural zeolites, has been under continuous development for several years. Synthetic zeolites often are cataloged by their Si/Al composition ratios, usually ranging from 1:1 to 10:500. Thus, aluminum plays a large role in this field. In the manufacture of synthetic zeolites, the common reactants are silica from sodium silicate (water-glass) or an aqueous colloidal silica, aluminum from sodium aluminate, alum, or a colloidal alumina (boehmite), and sodium or potassium hydroxide. For further detail, see the Vaughan (1988) reference.

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Additional Reading

Note: See list of references at end of next article.

ALUMINUM ALLOYS AND ENGINEERED MATERIALS. Aluminum alloys have been used effectively for scores of years. Much

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[2] Other atoms are used, but to a lesser extent, including Li, Be, B, Mg, Co, Mn, Zn, P, As, Ti, Ga, and Fe.

research during the past few decades has been directed not only to expand the list of alloys, but also for applying aluminum in other engineered forms, such as composites, sandwiched, and laminated materials. Aluminum fabrication and surface treatment have been improved. The techniques of powder metallurgy have been expanded to include the new engineering forms of aluminum. Aluminum quasi-crystals are a recent discovery. The "shape memory" of certain aluminum-base materials is being exploited. A process for using shock waves to shape aluminum also is among recent achievements.

Annually, sessions are held on *advanced aluminum alloys* as part of the conference on "Advanced Aerospace Materials/Processes and Exposition." Topics discussed have included rapid-solidification alloys, very low density alloys, laminates, new alloying elements, such as lithium, and such processes as diffusion bonding and means to improve fracture toughness and reduce fatigue and corrosion.

Aluminum is unique among the metals because it responds to nearly all of the known finishing processes. It can be finished in the softest, most delicate textures as exemplified by tableware and jewelry. Aluminum can be anodized and dyed to appear like gold. It can be made as specular as a silver mirror and jet black. The metal also can be anodized to an extremely hard, wear- and abrasion-resistant surface that approaches the hardness of a diamond. Aluminum is available in many convenient forms-shapes, sheet, plate, ingot, wire, rod and bar, foil, castings, forgings, powdered metals, and extrusions.

In the production of these products, new high-speed automated equipment has been developed over the past decade. Rolling speeds as high as 8000 feet (2438 meters) per minute are possible on some products. New continuous casting processes have been developed where molten metal can be converted directly into coiled sheet, using roll casting, belt casting, and articulated block casting. See Figs. 1 and 2. Many of the common alloys respond well to these new processes. Electromagnetic casting of the conventional giant ingots used for the conventional rolling mills has been developed in the fully automated mode. This casting process eliminates the need for scalping ingots prior to processing into final products, such as can stock, foil, auto body sheet, siding, and many other products. In this process, an electrical field rather than a solid mold wall is used to shape the ingot. The process is based upon the fact that liquids with good electrical conductivity, such as aluminum, can be constrained where an alternating magnetic field is applied. The liquid metal remains suspended by the electrical forces while it is being solidified.

The casting alloy products comprise sand castings, permanent mold castings, and die castings. Aluminum is the basic raw material for more than 20,000 businesses in the United States. Aluminum is an indispensable metal for aircraft, for example. See Fig. 3. Representative aluminum alloys for a broad classification of uses is given in Table 1.

Worldwide demand for aluminum over the past several decades has increased by approximately 5–6% per year. Aluminum is quite well established as an energy saver and a cost-effective material in numerous applications. Particularly strong growth is occurring in the automotive and transportation fields, housing, and food packaging. For example, a number of breakthroughs in foil pouch packaging have been achieved for replacing conventional cans for shelf-stable foods. Steady growth has continued in other areas, including aircraft and space applications, electrical wire and cable, marine, architectural, and consumer durable products. See Fig. 4.

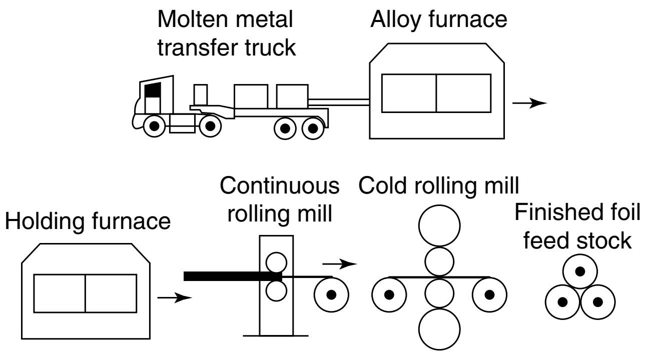

Fig. 1. Schematic portrayal of continuous aluminum roll casting process. (*Reynolds Metals Company.*)

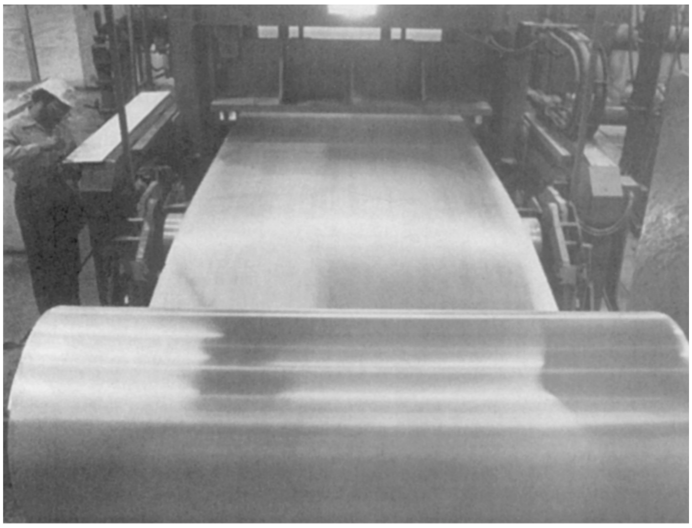

Fig. 2. Continuous rolling plant (Hot Spring, Arkansas) has cast nearly two billion pounds (0.9 billion kg) of aluminum foil feedstock since it began operations in 1979. That quantity of foil would wrap the earth almost 1600 times at the equator. The plant produces coils of feedstock for aluminum foil and flexible packaging products at a 40% energy saving compared to conventional rolling processes. (*Reynolds Metals Company.*)

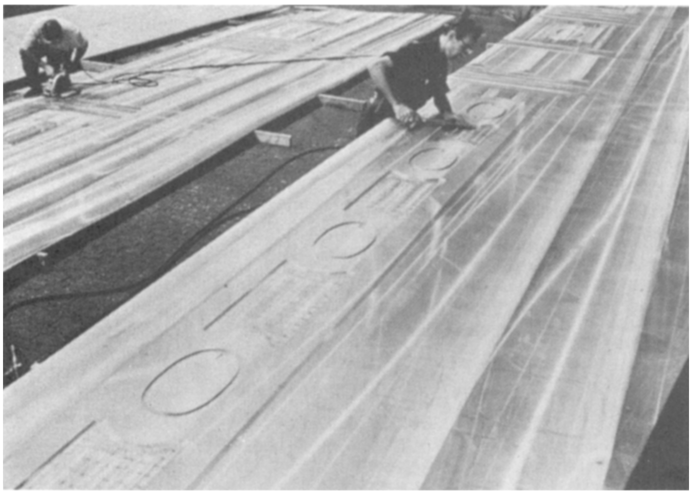

Fig. 3. Final operations on machined aluminum plates for wings of large jet aircraft. (*Reynolds Metals Company.*)

Pure aluminum is soft and ductile. In its annealed form, the tensile strength is approximately 13,000 pounds per square inch (90 megapascals). This can be work hardened by rolling, drawing into wire, or by other cold-working techniques to increase its strength to approximately 24,000 pounds per square inch (165 megapascals). Pure aluminum is particularly useful in the food and chemical industries where its resistance to corrosion and high thermal conductivity are desirable characteristics, and in the electrical industry, where its electrical conductivity of about 62% that of copper and its lightweight make it desirable for wire, cable, and bus bars. Large quantities are rolled to thin foils for the packaging of food products, for collapsible tubes, and for paste and powders used for inks and paints.

Most commercial uses require greater strength than pure aluminum affords. Higher strength is achieved by alloying other metal elements with aluminum and through processing and thermal treatments. The alloys can be classified into two categories, non-heat-treatable and heat-treatable.

TABLE 1. REPRESENTATIVE ALUMINUM ALLOYS

Product	Alloy	Form	Product	Alloy	Form
Architectural and Building Products					
Awnings	3003	Sheet			
Fence Wire	6061	Wire	Cable	E.C., 5005, 6201	Wire
Fittings	A514.0	Castings	Conduit	6063	Tubing
Gutters	Alc. 3004	Sheet	Motors	319.0, 355.0, 360.0,	Castings
Nails	5056, 6061	Wire		380.0	
Panels	3003, 6063	Sheet and Extrusions	Transmission Towers	6061, 6063, 7005	Extrusions
Roofing	Alc. 3004	Sheet	and Substations		
Screens	Alc. 5056	Wire	*Consumer Durables*		
Siding	3003, Alc. 3004	Sheet	Appliances	3003, 4343, 5052,	Sheet and
Transportation				5252, 5357, 5457	Extrusions
Aircraft	2014, 2024, 2048, 2090,		Sheet, Plate,		6063, 6463
	2124, 2219, 7075	Extrusions, and		356.0, 390.0	Castings
	7079, 7175, 7178,	Forgings	Cooking Utensils	1100, 3003, Alc. 3003,	Sheet
	7179, 7475, 8090, 8091,				3004, Alc. 3004, 5052,
	8092. B295.0, 355.0,	Castings		5454	
	356.0, 518.0,			B443.0, A514.0	Castings
	520.0		Furniture	3003, 3004, 5005,	Sheet and
Automotive				6463	Tubing
Auto and Truck	2036, 2037, 5052, 5182,	Sheet and	Refrigerators	3003, Alc. 3003, 3004,	Sheet and
Bodies	5252, 5657, 6009, 6010,	Extrusions		Alc. 3004, 4343, 5005,	Extrusions
	6061, 6063, 6463, 7016,			5050, 5052, 5252, 5457,	
	7021, 7029, 7046, 7129			6061, 6463	
Buses	2036, 5083, 5086,	Sheet and	Water Heaters	Alc. 6061, 3003	Sheet
	5182, 5252, 5457,	Extrusions	*Machinery and Equipment*		
	5657, 6061, 6063,		Chemical Processing	1060, 1100, 3003,	Sheet, Plate,
	6463, 7016, 7046			Alc. 3003, 3004,	Extrusions,
	242.0, B295.0,	Castings		Alc. 3004, 5083, 5086,	and Tubes
	355.0, 356.0,			5154, 5454, 6061, 6063	
	360.0, 380.0,			356.0, 360.0, B514.0	Castings
	390.0, B443.0		Heat exchangers and	3003, Alc. 3003, 3004,	Sheet and Tubing
Marine			Solar Panels	Alc. 3004, 4343, 5005,	
Barges, Small Craft,	5052, 5083, 5086,	Sheet, Plate,		5052, 6061, 6951	
Ships, Tankers	5454, 5456, 6061,	Extrusions, and	Sheet for Vacuum	4003, 4004, 4005,	
	6063	Tubing	Brazing Heat	4044, 4104	
	360.0, 413.0	Castings	Exchangers		
	B443.0		Irrigation	3003, Alc. 3003, 3004,	Tubing
Railroad	Alc. 2024, 5052,	Sheet, Plate,		Alc. 3004, 5052, 6061,	
	5083, 5086, 5454	and Extrusions		6063	
	5456, 6061, 6063, 7005		Sewage Plants	3003, Alc. 3003, 3004,	Sheet,
	B295.0, 356.0,	Castings		Alc. 3004, 5052, 5083,	Extrusions,
	520.0			5086, 5454, 5456, 6061,	and Tubes
Containers and Packaging				6063	
Foils	1100, 1235, 3003,	Foils		B514.0	Castings
	5005, 8079, 8111		Screw Machine Parts	2011, 2024, 6262	Rod and Bar
Cans	3003, 3004, 5182	Sheet	Textile Machinery	2014, 2024, 6061, 6063	Extrusions,
Electrical					Sheet and Plate
Bus Bar	6063, 6201	Extrusions or	*Finished Pressed Parts*	7090, 7091	Powder Metallurgy
		Rolled Rod			

Non-Heat-Treatable Alloys

The initial strength of alloys in this group depend upon the hardening effect of elements such as manganese, silicon, iron, and magnesium, singly or in various combinations (see three alloys in Table 2). The non-heat-treatable alloys are usually designated therefore in the 1xxx, 3xxx, 4xxx, and 5xxx series (Table 3). Since these alloys are work hardenable, further strengthening is made possible by various degrees of cold work denoted by the H series tempers.

Heat-Treatable Alloys. This group of alloys includes the alloying elements, copper, magnesium, zinc, and silicon (—T tempered alloys in Table 2). Since these elements singly or in combination show increasing solid solubility in aluminum with increasing temperature, it is possible to subject them to thermal treatments that will impart pronounced strengthening. The first step called heat treatment or solution heat treatment, is an elevated temperature process designed to put the soluble element or elements in solid solution. This is followed by a rapid quenching which momentarily "freezes" the structure and for a short time renders the alloy very workable. At room or elevated temperatures, the alloys are not stable after quenching, and precipitation of the constituent from the supersaturated solid solution begins. After several days at room temperature, termed aging or room temperature precipitation, the alloy is considerably stronger. Many alloys approach a stable condition at room temperature but some alloys, especially those containing magnesium and silicon or magnesium and zinc continue to age harden for long periods of time at room temperature. By heating for a controlled time at slightly elevated temperatures, even further strengthening is possible and the properties are stabilized.

Clad Alloys. The heat-treatable alloys, in which copper or zinc are major alloying constituents, are less resistant to corrosive attack than a majority of the non-heat-treatable alloys. To increase the corrosion resistance of these alloys in sheet and plate form, they are often clad with a high-purity aluminum, a low-magnesium-silicon alloy, or an aluminum alloy containing 1% zinc.

The cladding, usually from $2\frac{1}{2}$ to 5% of the total thickness on each side, not only protects the composite due to its own inherent excellent corrosion resistance, but also exerts a galvanic effect that further protects the core alloy.

Special composites may be obtained such as clad non-heat-treatable alloys for extra corrosion protection, for brazing purposes, and for special surface finishes.

Composites. The most commonly used metal elements alloyed with aluminum are magnesium, manganese, silicon, copper, zinc, iron, nickel, chromium, titanium, and zirconium. The strength of aluminum can be tailored to the specific end applications ranging from the very soft ductile foils to the high-strength aircraft and space alloys equal to steel in the 90,000 pounds per square inch (621 megapascals) tensile strength range. In addition to the homogeneous aluminum alloys, dispersion hardened and advanced filament-aluminum composites provide even higher strengths. Boron filaments in aluminum can provide strengths in the range of 150,000–300,000 pounds per square inch (1034–2068 megapascals) tensile strength.

Superplasticity. Eutectoid and near eutectoid alloy chemistry research has resulted in alloys exhibiting superplasticity with unusual elongation (>1000%) and formability and with 60,000 pounds per square inch (414 megapascals) tensile strength. Three examples of these alloys are: 94.5% A1-5% Cu-0.5% Zr; 22% A1-78% Zn; and 90% A1, 5% Zn, 5% Ca.

Casting Alloys

During the last two decades, the quality of castings has been improved substantially by the development of new alloys and better liquid-metal treatment and also by improved casting techniques. Casting techniques include sand casting, permanent mold casting, pressure die casting, and others. Today sand castings can be produced in high-strength alloys and are weldable. Die casting permits large production outputs per hour on intricate pieces that can be cast to close dimensional tolerance and have excellent surface finishes; hence, these pieces require minimum machining. Since aluminum is so simple to melt and cast, a large number of foundry shops have been established to supply the many end products made by this method of fabrication. See Table 3.

Al_2O_3, Casting Semisolid Metal. A new casting technology is based on vigorously agitating the molten metal during solidification. A very different metal structure results when this metal is cast. The vigorously agitated liquid-solid mixture behaves as a slurry still sufficiently fluid (thixotropic) to be shaped by casting. The shaping of these metal slurries is termed "Rheocasting."

The slurry nature of "Rheocast" metal permits addition and retention of particulate nonmetal (e.g., Al_2O_3, SiC, T, C, glass beads) materials for cast composites. This new technology is beginning to be commercialized.

Alloy and Temper Designation Systems for Aluminum. The aluminum industry has standardized the designation systems for wrought aluminum alloys, casting alloys and the temper designations applicable. A system of four-digit numerical designations is used to identify wrought aluminum alloys. The first digit indicates the alloy group as shown in Table 4. The 1xxx series is for minimum aluminum purities of 99.00% and greater; the last two of the four digits indicate the minimum aluminum percentage; i.e., 1045 represents 99.45% minimum aluminum, 1100 represents 99.00%

Fig. 4. Four aluminum sections of this type make up fuel tank for aerospace vehicle. Each section is produced from computer-machined plate and weighs 4750 pounds (2155 kg). (*Reynolds Metals Company*)

TABLE 2. NOMINAL CHEMICAL COMPOSITION[1] AND TYPICAL PROPERTIES OF SOME COMMON ALUMINUM WROUGHT ALLOYS PTV

	1100	3003	5052	2014T6[10]	2017T4[9]	2024T4[9]	6061T6[10]	7075T6[10]	6101T6[10]
Nominal chemical Composition[1]	99% Min. Alum.	1.2% Mn	2.5% Mg 0.25% Cr	4.4% Cu 0.8% Si 0.8% Mn 0.4% Mg	4.0% Cu 0.5% Mn 0.5% Mg	4.5% Cu 1.5% Mg 0.6% Mn	1.0% Mg 0.6% Si 0.25% Cu 0.25% Cr	5.5% Zn 2.5% Mg 1.5% Cu 0.3% Cr	0.5% Mg 0.5% Si
Tensile strength, psi	A 13,000[7]	16,000	28,000	—	—	—	—	—	—
	H 24,000[7]	29,000	42,000	70,000	62,000	68,000	45,000	83,000	32,000
Tensile strength, MPa	A 90	110	193	—	—	—	—	—	—
	H 165	200	290	483	427	469	310	572	221
Yield strength, psi[2]	A 5000	6000	13,000	—	—	—	—	—	—
	H 22,000	27,000	7,000	60,000	40,000	47,000	40,000	73,000	28,000
Yield strength, Mpa	A 34	41	90	—	—	—	—	—	—
	H 152	186	255	414	276	324	276	503	193
Elongation percent	A 45	A 40	A 30	13	22	19	17	11	15
in 2 in. (5.1 cm)11	H 15	H 10	H 8						
Modulus of elasticity[3]	10	10	10.2	10.6	10.5	10.6	10	10.4	10
Brinnell hardness[8]	23–44	28–55	45–85	135	105	120	95	150	71
Melting range,°C	643–657	643–654	593–649	510–638	513–640	502–638	582–652	477–638	616–651
Melting range,°F	1190–1215	1190–1210	1100–1200	950–1180	955–1185	935–1180	1080–1250	890–1180	1140–1205
Specific gravity	2.71	2.73	2.68	2.80	2.79	2.77	2.70	2.80	2.70
Electrical resistivity[4]	2.9	3.4	4.93	4.31	5.75	5.75	4.31	5.74	3.1
Thermal conductivity[5]	0.53	A 0.46	A 0.33	0.37	0.29	0.29	0.37	0.29	0.52
SI units	221.9	A 192.6	A 138.2	154.9	121.4	121.4	154.9	121.4	217.7
Coefficient of expansion[6]	23.6	23.2	23.8	22.5	23.6	22.8	23.4	23.2	23

[1] Aluminum plus normal impurities is the remainder.

[2] 0.2% permanent set.

[3] Multiply by 10^6.

[4] Microhms per cm (room temperature).

[5] C.g.s. units (at 100°C).

[6] Per°C (20–100°C); multiply by 10^{-6}.

[7] A = annealed; H = hard.

[8] 500 kg load, 10 mm ball.

[9] Solution heat-treated and naturally aged.

[10] Solution heat-treated and artificially aged.

[11] Round specimens, $\frac{1}{2}$-m diameter.

Conversion factors used: 1 psi = 6.894757 × 10^{-3} megapascals (MPa).

C.g.s. = (cal) (cm^2)/(sec)(cm)(°C).

SI unit = Watts/meter °K.

1 C.g.s. unit = 418.68 SI units.

minimum aluminum. The 2xxx through 8xxx series group aluminum alloys by major allowing elements. In these series the first digit represents the major alloying element, the second digit indicates alloy modification, while the third and fourth serve only to identify the different alloys in the group. Experimental alloys are prefixed with an X. The prefix is dropped when the alloy is no longer considered experimental.

Cast Aluminum Alloy Designation System. A four-digit number system is used for identifying aluminum alloys used for castings and foundry ingot (see Table 5). In the 1xx.x group for aluminum purity of 99.00% or greater, the second and third digit indicate the minimum aluminum percentage. The last digit to the right of the decimal point indicates the product form: 1xx.0 indicates castings and 1xx.1 indicates ingot. Special control of one or more individual elements other than aluminum is indicated by a serial letter before the numerical designation. The serial letters are assigned in alphabetical sequence starting with A but omitting I, O, Q, and X, the X being reserved for experimental alloys.

In the 2xx.x through 9xx.x alloy groups, the second two of the four digits in the designation have no special significance but serve only to identify the different aluminum alloys in the group. The last digit to the right of the decimal point indicates the product form: .0 indicates casting and .1 indicates ingot. Examples: Alloy 213.0 represents a casting of an aluminum alloy whose major alloying element is copper. Alloy C355.1 represents the third modification of the chemistry of an aluminum alloy ingot whose major alloying elements are silicon, copper, and magnesium.

Temper Designation System. A temper designation is used for all forms of wrought and cast aluminum alloys. The temper designation follows the alloy designation, the two letters being separated by a hyphen. Basic designations consist of letters followed by one or more digits. These designate specific sequences of basic treatments but only operations recognized as significantly influencing the characteristics of the product. Basic tempers are −F (as fabricated), −O annealed (wrought products only), −H strain-hardened (degree of hardness is normally quarter hard, half hard, three-quarters hard, and hard, designated by the symbols H12, H14, H16, and H18, respectively). −W solution heat-treated and −T thermally treated to produce stable tempers. Examples: 1100-H14 represents commercially pure aluminum cold rolled to half-hard properties. 2024-T6 represents an aluminum alloy whose principal major element is copper that has been solution heat treated and then artificially aged to develop stable full-strength properties of the alloy.

Contemporary Advancements and Future Potential

Highlighted in the following paragraphs are improvements in aluminum metallurgy that have occurred and have been available only relatively recently or that are promising but that still remain in a late phase of research or testing.

Aluminum-Lithium Alloys. Both private and government funding have been invested in Al−Li alloy research for several years. As of the early 1990s, exceptionally good results had been achieved by way of increasing the strength-to-weight ratio and the stiffness of Al−Li alloys. Low ductility in the short-transverse direction has been a difficult problem to solve. Wide usage awaits further problem solving and testing for critical applications. The Al−Li alloy 2091-T3 (Pechiney) is a medium-strength, lightweight alloy quite similar to the traditional alloy 2024-T3, which it is expected to

TABLE 3. NOMINAL CHEMICAL COMPOSITION[1] AND TYPICAL PROPERTIES OF SOME ALUMINUM CASTING ALLOYS

Properties for alloys 195, B195, 220, 355, and 356 are for the commonly used heat treatment

	413.0[2]	B443.0[2]	208.0[3]	308.0[4]	295.0[3]	B295.0[4]	514.0[3]	518.0[2]	520.0[3]	355.0[3]	356.0[3]	380.0[2]
Nominal chemical composition	12% Si	5% Si	4% Cu	5.5% Si 3% Si	4.5% Cu 4.5% Cu	4.5% Cu 0.8% Si	3.8% Mg 2.5% Si	8% Mg	10% Mg	5% Si	7% Si 0.5% Mg	8.5% Si
Tensile strength, psi[5]	37,000	19,000	21,000	28,000	36,000	45,000	25,000	42,000	46,000	35,000	33,000	45,000
Tensile strength, Mpa[5]	255	131	145	193	248	310	172	290	317	241	228	310
Yield strength, psi[5]	18,000	9000	14,000	16,000	24,000	33,000	12,000	23,000	25,000	25,000	24,000	25,000
Yield strength, Mpa[5]	124	62	97	110	165	228	83	159	174	174	165	174
Elongation, percent[5]	1.8	6	2.5	2	5	5	9	7	14	2.5	4	2
Brinnell hardness[6]	—	40	55	70	75	90	50	—	75	80	70	—
Melting range,°C	574–585	577–630	521–632	—	549–646	527–627	580–640	540–621	449–621	580–627	580–610	521–588
Melting range,°F	1065–1085	1070–1165	970–1170	—	1020–1195	980–1160	1075–1185	1005–1150	840–1150	1075–1160	1075–1130	970–1090
Specific gravity	2.66	2.69	2.79	2.79	2.81	2.78	2.65	2.53	2.58	2.70	2.68	2.76
Electrical resistivity	4.40	4.66	5.56	4.66	4.66	3.45	4.93	7.10	8.22	4.79	4.42	6.50
Thermal conductivity	70.37	0.35	0.29	0.34	0.35	0.45	0.33	0.24	0.21	0.34	0.36	0.26
SI units	154.9	146.5	121.4	142.4	146.5	188.4	138.2	100.5	87.9	142.4	150.7	108.9
Coefficient of expansion	820.0	22.8	22.8	22.7	23.9	22.8	24.8	24.0	25.4	22.8	22.8	20.0

[1] Remainder is aluminum plus minor impurities.

[2] Die cast.

[3] Sand cast.

[4] Permanent mold cast.

[5] For separately cast test bars.

[6] 500 kg/load, 10 mm, ball.

[7] C.g.s. units.

[8] Multiply by 10^{-6}. Per°C, for temperature range 20 to 200°C.

Conversion factors used: 1 psi = 6.894757×10^{-3} megapascals (MPa).

SI unit = Watts/meter °K.

1 C.g.s. unit = 418.68 SI units.

replace for aerospace applications. The new alloy has a 7% lower density and a 10% higher stiffness. The new alloy, like most Al alloys, is notch sensitive. An oxide film composed of MgO, LiO_2, $LiAlO_2$, Li_2CO_3, and LiOH tends to develop under normal production conditions. Cracks form in this film and tend to initiate cracks in the alloy's substrate and this reduces fatigue life. When the film is removed, in both longitudinal and long-transverse directions, the new alloy's fatigue properties are comparable with other aluminum alloys.

In late 1989, the availability of a proprietary family of weldable, high-strength (*Weldalite*) Al—Li products appeared. The material was claimed to be nearly twice as strong (100×10^3 psi) as other leading alloys then currently used for aerospace applications. The alloy was initially developed especially for space-launch systems. Specific advantages claimed include: (1) high strength over a broad temperature range, from cryogenic to highly elevated temperatures, (2) light weight, and (3) weldability—this property being of particular value for fabricating fuel and oxidizer tanks for space vehicles. *Weldalite* is produced in sheet, plate, extrusion, and ingot products.

TABLE 4. DESIGNATIONS FOR CAST ALUMINUM ALLOY GROUPS

Alloy No.		
Aluminium-99.00% minimum and greater		1xxx
MAJOR ALLOYING ELEMENT		
Aluminium Alloys Grouped by Major Alloying Elements	Copper	2xxx
	Manganese	3xxx
	Silicon	4xxx
	Magnesium	5xxx
	Magnesium and Silicon	6xxx
	Zinc	7xxx
	Other Element	8xxx
Unused Series		9xxx

(1) For codification purposes an alloying element is any element which is intentionally added for any purpose other than grain refinement and for which minimum and maximum limits are specified.

(2) Standard limits for alloying elements and impurities are expressed to the following places:

Less than 1/1000%	0.000X
1/1000 up to 1/100%	0.00X
1/100 up to 1/10%	
Unalloyed aluminum made by a refining process	0.0XX
Alloys and unalloyed aluminum not made by a refining process	0.0X
1/10 through 1/2%	0.XX
Over 1/2%	0.X, X.X, etc.

Al—Li investment castings are gaining acceptance. Among aluminum alloying elements, lithium is one of the most soluble. About 4.2% Li can be dissolved in Al at the eutectic temperature, 1116°F (602°C). However, in commercial-size ingots, the maximum Li content that can be cast without cracking is about 2.7%. Lithium is a strengthening element because of the formation of small, coherent ordered Al_3Li precipitates during aging (secondary hardening when Li content exceeds 1.4%). The toughness of Al—Li alloys, unlike conventional Al alloys, does not increase with increasing aging temperature (beyond that point needed for peak strength).

Metal-Matrix Composites. Silicon carbide particles are contributing to easy-to-cast metal-matrix composites (MMCs). When compared with their non-reinforced counterparts, the SiCp/Al components are more wear resistant, stiffer, and stronger, accompanied by improved thermal stability. Additional advantages include lower density and lower cost. Nearly all prior aluminum MMCs required labor-intensive methods, such as powder metallurgy, diffusion bonding, squeeze casting, or thermal spraying.

The new SiC composites are available as foundry ingot or extrusion billets. A new process ensures complete wetting of the SiC particles by molten aluminum. A number of investment castings are now being made, including aircraft hydraulic components and other small parts. These composites have excellent prospects for use in a variety of small parts, including medical prostheses and golf club heads.

Sialons consist of three-dimensional arrays of (Si—Al) $(O,N)_4$ tetrahedra. These oxynitrides are traditionally fabricated with silicon nitride. An example is beta-sialon, where the O and Si are partially replaced by N and Al, respectively. Advanced sialons are now being researched to enhance fracture toughness and improved creep properties.

Aluminides. These are intermetallic compounds of aluminum. The potential of these products includes uses where low weight, high-temperature strength, and oxidation resistance are required. Traditionally, these products are made by way of powder metallurgy technology.

TABLE 5. DESIGNATIONS FOR CAST ALUMINUM ALLOY GROUPS

	Alloy No.	
Aluminum	99.00% minimum and greater	1xx.x
	Major Alloy Element	
	Copper	2xx.x
Aluminum	Silicon, with added Copper	
Alloys	and/or Magnesium	3xx.x
Grouped	Silicon	4xx.x
By Major	Magnesium	5xx.x
Alloying	Zinc	7xx.x
Elements	Tin	8xx.x
	Other Element	9xx.x
Unused Series		6xx.x

(1) For codification purposes an alloying element is any element which is intentionally added for any purpose other than grain refinement and for which minimum and maximum limits are specified.

(2) Standard limits for alloying elements and impurities are expressed to the following places:

Less than 1/1000%	0.000X
1/1000 up to 1/100%	0.00X
1/100 up to 1/10%	
Unalloyed aluminum made by a refining process	0.0XX
Alloys and unalloyed aluminum not made by a refining process	0.0X
1/10 through 1/2%	0.XX
Over 1/2%	0.X, X.X, etc.

Powder consolidation has been affected by sintering and hot isostatic pressing, both methods requiring long processing at height temperature. They rely mainly on solid-state diffusion. In a more recent method, *dynamic consolidation* uses high-pressure shock waves traveling at several kilometers per second. Such shocks can be generated through the use of detonating explosives or a gun-fired projectile. Upon full development of the shock-wave technique, advantages predicted include: (1) the non-equilibrium microstructures produced in rapid-solidification processing of powders will be retained in the final compact, (2) composite materials may be fabricated with very thin reaction zones between matrix and reinforcement, thus minimizing brittle reaction products that distract from the composite properties, and (3) net shapes may be produced. Normally confined in the past to production of centimeter-size parts, an improved process may be scaled up to meter-size products. Further development is required to prevent the formation of cracks.

Shape-Memory Alloys. Stoeckel defines a shape-memory alloy as the ability of some plastically deformed metals (and plastics) to resume their original shape upon heating. This effect has been observed in numerous metal alloys, notably the Ni−Ti and copper-based alloys, where commercial utilization of this effect has been exploited. (An example is valve springs that respond automatically to change in transmission-fluid temperature.) Copper-based alloy systems also exhibit this effect. These have been Cu−Zn−Al and Cu−Al−Ni systems. In fact, the first thermal actuator to utilize this effect (a greenhouse window opener) uses a Cu−Zn−Al spring.

ARALL Laminates

Developed in the late 1970s, *AR*amid *AL*uminum *L*aminates were developed by Delft University and Fokker Aircraft Co. The laminate currently is used for the skin of the cargo door for the Douglas C-17 military transport aircraft, but additional aerospace applications are envisioned. In essence, the laminate comprises a prepreg (i.e., unidirectional aramid fibers embedded in a structural epoxy adhesive) sandwiched between layers of aircraft alluminum alloy sheet. The fibers are oriented parallel to the rolling direction of the aluminum sheet. Prior to lay-up and autoclave curing, the aluminum surfaces are anodized and primed to ensure good bond integrity and to inhibit corrosion of the metal in the event of moisture intrusion at the bond line.

Quasicrystals

In the early 1980s, D. Schechtman at NIST (U.S. Nat ional Institute for Standards and Technology) discovered quasicrystals in aluminum alloys. Since then, they also have been noted in other alloys, including those of copper, magnesium, and zinc. Quasicrystals contradict the traditional fundamentals of crystallography to the effect that the periodicity of a perfect crystal structure is not possible with pentagon shapes. Much pioneering research on quasicrystals also has been conducted at the Laboratoire de Science at Gènie des Matèriaux Mètalliques in France.

To date, little use has been found for quasicrystals in bulk, but they have proved very effective as coatings, notably in cookware. Recent cookware, with a different appearance and "feel," has appeared in the marketplace. These pots, pans, and so on, have a hardness equal to that of hardened alloy steel and thus are practically immune to scratching. They also are thermally stable and corrosion and oxidation resistant.

The coating is applied by using flame, supersonic, and plasma-arc spraying. The deposited material consists of a mixture of quasicrystals and crystalline phases. The quasicrystal content of the surface ranges from 30−70%.

In structure, the quasicrystal relates to the Penrose tile structures (polygon), originally proposed by Roger Penrose, a mathematician at Oxford University. See **Crystal**.

Advances in Powdered Metallurgy (PM) Aluminum Alloys

As noted by Frazier, materials for advanced airframe structures and propulsion systems must withstand increasingly high temperature exposure. For example, frictional heating can raise supersonic skin temperatures to a range of 555° to 625°F (290° to 330°C). Unfortunately, wrought age-hardening aluminum alloys lose strength above 265°F (130°C). Titanium alloys perform well under these conditions, but they are 67% denser than aluminum, constituting about 42% of the weight of contemporary turbofan engines. Replacement of half the titanium with aluminum would reduce engine weight by about 20%. The motivation for using PM products is cost reduction and improved performance. Advanced thermoplastic matrix composites under development are difficult to process and presently cost prohibitive. Thus, intensive research is underway to improve rapid solidification technology and other new PM processes to increase the alloy aluminum content, thus reducing weight and cost.

Aluminum Electroplating

Electroplated aluminum is growing in acceptance for use in automotive parts, electrical equipment, and appliances and for products in a marine environment. Markets may be extended as the result of a new galvano-aluminum electroplating process developed by Siemens Research Laboratory (Erlangen, Germany) and described in the Hans reference.

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ALUNITE. The mineral alunite, $KAl_3(SO_4)_2(OH)_6$, is a basic hydrous sulfate of aluminum and potassium; a variety called natroalunite is rich in soda. Alunite crystallizes in the hexagonal system and forms rhombohedrons with small angles, hence resembling cubes. It may be in fibrous or tabular forms, or massive. Hardness, 3.5–4; sp gr, 2.58–2.75; luster, vitreous to pearly; streak white; transparent to opaque; brittle; color, white to grayish or reddish.

Alunite is commonly associated with acid lava due to sulfuric vapors often present; it may occur around fumaroles or be associated with sulfide ore bodies. It has been used as a source of potash. Alunite is found in the Czech Republic and Slovakia, Italy, France, and Mexico; in the United States, in Colorado, Nevada, and Utah.

Alunite is also known as *alumstone*.

AMALGAM. 1. An alloy containing mercury. Amalgams are formed by dissolving other metals in mercury, when combination takes place often with considerable evolution of heat. Amalgams are regarded as compounds of mercury with other metals, or as solutions of such compounds in mercury. It has been demonstrated that products which contain mercury and another metal in atomic proportions may be separated from amalgams. The most commonly encountered amalgams are those of gold and silver. See also **Gold**; **Mercury**; and **Silver**.

2. A naturally occurring alloy of silver with mercury, also referred to as mercurian silver, silver amalgam, and argental mercury. The natural amalgam crystallizes in the isometric system; hardness, 3–3.5; sp gr, 13.75–14.1; luster, metallic; color, silver-white; streak, silver-white; opaque. Amalgam is found in Bavaria, British Columbia, Chile, the Czech Republic and Slovakia, France, Norway, and Spain. In some areas, it is found in the oxidation zone of silver deposits and as scattered grains in cinnabar ores.

AMBER. Amber is a fossil resin known since early times because of its property of acquiring an electric charge when rubbed. In modern times it has been used largely in the making of beads, cigarette holders, and trinkets. Its amorphous non-brittle nature permits it to be carved easily and to acquire a very smooth and attractive surface. Amber is soluble in various organic solvents, such as ethyl alcohol and ethyl ether.

It occurs in irregular masses showing a conchoidal fracture. Hardness, 2.25; sp gr, 1.09; luster, resinous; color, yellow to reddish or brownish; it may be cloudy. Some varieties will exhibit fluorescence. Amber is transparent to translucent, melts between 250 and 300°C.

Amber has been obtained for over 2,000 years from the lignite-bearing Tertiary sandstones on the coast of the Baltic Sea from Gdansk to Liepàja; also from Denmark, Sweden and the other Baltic countries. Sicily furnishes a brownish-red amber that is fluorescent.

The association of amber with lignite or other fossil woods, as well as the beautifully preserved insects that are occasionally in it, is ample proof of its organic origin.

AMBERGRIS. A fragrant waxy substance formed in the intestine of the sperm whale and sometimes found floating in the sea. It has been used in the manufacture of perfumes to increase the persistence of the scent.

AMBLYGONITE. A rather rare compound of fluorine, lithium, aluminum, and phosphorus, $(Li, Na)AlPO_4(F, OH)$. It crystallizes in the tri-clinic system; hardness, 5–5.6; sp gr 3.08; luster, vitreous to greasy or pearly; color, white to greenish, bluish, a yellowish or grayish; streak white; translucent to subtransparent.

Amblygonite occurs in pegmatite dikes and veins associated with other lithium minerals. It is used as a source of lithium salts. The name is derived from two Greek words meaning blunt and angle, in reference to its cleavage angle of $75°30'$.

Amblygonite is found in Saxony; France; Australia; Brazil; Varutrask, Sweden; Karibibe, S.W. Africa; and the United States.

AMERICIUM. [CAS: 7440-35-9]. Chemical element, symbol Am, at no. 95, at. wt. 243 (mass number of the most stable isotope), radioactive metal of the actinide series, also one of the transuranium elements. All isotopes of americium are radioactive; all must be produced synthetically. The element was discovered by G.T. Seaborg and associates at the Metallurgical Laboratory of the University of Chicago in 1945. At that time, the element was obtained by bombarding uranium-238 with helium ions to produce ^{241}Am, which has a half-life of 475 years. Subsequently, ^{241}Am has been produced by bombardment of plutonium-241 with neutrons in a nuclear reactor. ^{243}Am is the most stable isotope, an alpha emitter with a half-life of 7950 years. Other known isotopes are ^{237}Am, ^{238}Am, ^{240}Am, ^{241}Am, ^{242}Am, ^{244}Am, ^{245}Am, and ^{246}Am. Electronic configuration is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}5f^76s^26p^67s^2$. Ionic radii are: Am^{4+}, 0.85 Å; Am^{3+}, 1.00Å.

This element exists in acidic aqueous solution in the (III), (IV), (V), and (VI) oxidation states with the ionic species probably corresponding to Am^{3+}, Am^{4+}, AmO_2^+ and AmO_2^{2+}.

The colors of the ions are: Am^{3+}, pink; Am^{4+}, rose; AmO_2^+, yellow; and AmO_2^{2+}, rum-colored.

It can be seen that the (III) state is highly stable with respect to disproportionation in aqueous solution and is extremely difficult to oxidize or reduce. There is evidence for the existence of the (II) state since tracer amounts of americium have been reduced by sodium amalgam and precipitated with barium chloride or europium sulfate as carrier. The (IV) state is very unstable in solution: the potential for americium(III)-americium(IV) was determined by thermal measurements involving solid AmO_2. Americium can be oxidized to the (V) or (VI) state with strong oxidizing agents, and the potential for the americium(V)-americium(VI) couple was determined potentiometrically.

In its precipitation reactions americium(III) is very similar to the other tripositive actinide elements and to the rare earth elements. Thus the fluoride and the oxalate are insoluble and the phosphate and iodate are only moderately soluble in acid solution, whereas the nitrates, halides, sulfates, sulfides, and perchlorates are all soluble. Americium(VI) can be precipitated with sodium acetate giving crystals isostructural with sodium uranyl acetate,

$$NaUO_2(C_2H_3O_2)_3 \cdot xH_2O$$

and the corresponding neptunium and plutonium compounds.

Of the hydrides of americium, both AmH_2 and Am_4H_{15} are black and cubic.

When americium is precipitated as the insoluble hydroxide from aqueous solution and heated in air, a black oxide is formed which corresponds almost exactly to the formula AmO_2. This may be reduced to $Am_2 O_3$ through the action of hydrogen at elevated temperatures. The AmO_2 has the cubic fluorite type structure, isostructural with UO_2, NpO_2, and PuO_2. The sesquioxide, $Am_2 O_3$ is allotropic, existing in a reddish brown and a tan form, both hexagonal. As in the case of the preceding actinide elements, oxides of variable composition between $AmO_{1.5}$ and AmO_2 are formed depending upon the conditions.

All four of the trihalides of americium have been prepared and identified. These are prepared by methods similar to those used in the preparation of the trihalides of other actinide elements. AmF_3 is pink and hexagonal, as is $AmCl_3$; $AmBr_3$ is white and orthorhombic; while a tetrafluoride, AmF_4 is tan and monoclinic.

In research at the Institute of Radiochemistry, Karlsruhe, West Germany during the early 1970s, investigators prepared alloys of americium with platinum, palladium, and iridium. These alloys were prepared by hydrogen reduction of the americium oxide in the presence of finely divided noble metals according to:

$$Am_2O_3 + 10Pt \xrightarrow[1100^\circ C]{H_2} 2\ AmPt_5 + H_2O$$

The reaction is called a *coupled reaction* because the reduction of the metal oxide can be done only in the presence of noble metals. The hydrogen must be extremely pure, with an oxygen content of less than 10^{-25} torr.

See also **Chemical Elements**.

Industrial utilization of americium has been quite limited. Uses include a portable source for gamma radiography, a radioactive glass thickness gage for the flat glass industry, and an ionization source for smoke detectors.

Americium is present in significant quantities in spent nuclear reactor fuel and poses a threat to the environment. A group of scientists at the U.S. Geological Survey (Denver, Colorado) has studied the chemical speciation of actinium (and neptunium) in ground waters associated with rock types that have been proposed as possible hosts for nuclear waste repositories. Researchers Cleveland, Nash, and Rees (see reference list) concluded that americium (and neptunium) are relatively insoluble in ground waters containing high sulfate concentrations (90°C).

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AMERICAN ASSOCIATION OF SCIENTIFIC WORKERS (AASW). Founded in 1946. Scientists concerned with national and international relations of science and society and with organizational aspects of science. It is located at the School of Veterinary Medicine, University of Pennsylvania, Philadelphia, PA 19172.

AMERICAN ASSOCIATION OF TEXTILE CHEMISTS AND COLORISTS (AATCC). Founded in 1921. It has over 6500 members. A technical and scientific society of textile chemists and colorists in textile and related industries using colorants and chemical finishes. It is the authority for test methods. It is located at PO Box 12215, Research Triangle Park, NC 27709. http://www.aatcc.org/

AMERICAN CARBON SOCIETY (ACS). The present name of the American Carbon Committee, a group incorporated in 1964 to operate the Biennial American Carbon Conferences. The committee also has sponsored the international journal *Carbon*. Over 500 members (physicist, chemists, technicians, and other scientific personnel) worldwide focus on the physics and chemistry of organic crystals, polymers, chars, graphite, and carbon materials. It is located at the Stackpole Corporation, St. Mary's, PA 19174. http://www.americancarbonsociety.org/

AMERICAN CERAMIC SOCIETY (ACerS). Founded 1899. It has 12,000 members. A professional society of scientists, engineers, and plant operators interested in glass, ceramics-metal systems, cements, refractories, nuclear ceramics, white wares, electronics, and structural clay products. It is located at 65 Ceramic Dr., Columbus, OH 43214. http://www.acers.org/

AMERICAN CHEMICAL SOCIETY (ACS). Founded in 1876. It has over 150,000 members. The nationally chartered professional society for chemists in the U.S. One of the largest scientific organizations in the world. Its offices are at 1155 16th St., NW, Washington DC 20036. http://www.acs.org/

AMERICAN INSTITUTE OF CHEMISTS (AIC). Founded in 1923, it is primarily concerned with chemists and chemical engineers as professional people rather than with chemistry as a science. Special emphasis is placed on the scientific integrity of the individual and on a code of ethics adhered to by all its members. It publishes a monthly journal, *The Chemist*. It is located at 7315 Wisconsin Ave, NW, Bethesda, MD 20814. http://www.theaic.org/

AMERICAN NATIONAL STANDARDS INSTITUTE (ANSI). Founded in 1918. A federation of trade associations, technical societies, professional groups, and consumer organizations that constitutes the U.S. clearinghouse and coordinating body of voluntary standards activity on the national level. It eliminates duplication of standards activities and combines conflicting standards into single, nationally accepted standards. It is the U.S. member of the International Organization for Standardization and the International Electrotechnical Commission. Over 1000 companies are members of the ANSI. One of its primary concerns is safety in such fields as hazardous chemicals, protective clothing, welding, fire control, electricity and construction operations, blasting, etc. Its address is 1430 Broadway, New York, NY 10018. http://www.ansi.org/

AMERICAN OIL CHEMIST'S SOCIETY (AOCS). Founded in 1909. It has over 5000 members. These members are chemists, biochemists, chemical engineers, research directors, plant personnel, and persons concerned with animal, marine, and regular oils and fats and their extraction, refining, safety, packaging, quality control, and use. The address is 508 S. 6th St., Champaign, IL 61820. http://www.aocs.org/

AMERICAN PETROLEUM INSTITUTE (API). Founded in 1919. It has 5500 members. The members are the producers, refiners, marketers, and transporters of petroleum and allied products such as crude oil, lubricating oil, gasoline, and natural gas. The address is 1220 L Street, NW. Washington, DC 20005-4070. http://www.api.org

AMERICAN SOCIETY FOR METALS (ASM). Formally organized in 1935, this society actually had been active under other names since 1913, when the need for standards of metal quality and performance in the automobile became generally recognized. ASM has over 53,000 members and publishes *Metals Review* and the famous *Metals Handbook*, as well as research monographs on metals. It is active in all phases of metallurgical activity, metal research, education, and information retrieval. Its headquarters is at Metals Park, OH, 44073. http://www.asm.org/

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM). This society, organized in 1898 and chartered in 1902, is a scientific and technical organization formed for "the development of standards on characteristics and performance of materials, products, systems and services, and the promotion of related knowledge." There are over 31,000 members. It is the world's largest source of voluntary consensus standards. The society operates via more than 125 main technical committees that function in prescribed fields under regulations that ensure balanced representation among producers, users, and general-interest participants. Headquarters of the society is at 655 15th St., Washington DC 2005. http://www.astm.org/

AMETHYST. A purple- or violet-colored quartz having the same physical characteristics as quartz. The source of color is not definite but thought to be caused by ferric iron contamination. Oriental amethysts are purple corundum.

Amethysts are found in the Ural Mountains, India, Sri Lanka, Madagascar, Uruguay, Brazil, the Thunder Bay district of Lake Superior in Ontario, and Nova Scotia; in the United States, in Michigan, Virginia, North Carolina, Montana, and Maine.

The name amethyst is generally supposed to have been derived from the Greek word meaning not drunken. Pliny suggested that the term was applied because the amethyst approaches but is not quite the equivalent of a wine color.

See also **Quartz**.

AMIDES. An amide may be defined as a compound that contains the $CO\cdot NH_2$ radical, or an acid radical(s) substituted for one or more of the hydrogen atoms of an ammonia molecule. Amides may be classified as (1) *primary amides*, which contain one acyl radical, such as $-CO\cdot CH_3$ (acetyl) or $-CO\cdot C_6H_5$ (benzoyl), linked to the *amido* group ($-NH_2$). Thus, acetamide NH_2COCH_3 is a combination of the acetyl and amido groups; (2) *secondary amides*, which contain two acyl radicals and the *imido* group ($-NH_2$) Diacetamide $HN(COCH_3)_2$ is an example; and (3) *tertiary amides*, which contain three acyl radicals attached to the N atom. Triacetamide $N(COCH_3)_3$ is an example.

A further structural analysis will show that amides may be regarded as derivatives of corresponding acids in which the amido group substitutes for the hydroxyl radical OH of the carboxylic group COOH. Thus, in the instance of formic acid HCOOH, the amide is $HCOONH_2$ (formamide); or in the case of acetic acid CH_3 COOH, the amide is CH_3 $CONH_2$ (acetamide). Similarly, urea may be regarded as the amide of carbonic acid (theoretical) O:C, that is, NH_2 $CONH_2$ (urea). The latter represents a dibasic acid in which two H atoms of the hydroxyl groups have been replaced by amido groups. A similar instance, malamide,

$$NH_2CO\cdot CH_2CH(OH)\cdot CONH_2$$

is derived from the dibasic acid, malic acid,

$$OHCO\cdot CH_2CH(OH)\cdot COOH.$$

Aromatic amides, sometimes referred to as *arylamides*, exhibit the same relationship. Note the relationship of benzoic acid C_6 H_5 COOH with benzamide C_6 H_5 $CONH_2$. *Thiamides* are derived from amides in which there is substitution of the O atom by a sulfur atom. Thus, acetamide $NH_2\cdot$ CO$\cdot$ CH_3, becomes thiacetamide $NH_2\cdot$ CS$\cdot$ CH_3; or acetanilide C_6 $H_5\cdot$ NH$\cdot$ CO$\cdot$ CH_3 becomes thiacetanilide C_6 $H_5\cdot$ NH$\cdot$ CS$\cdot$ CH_3. *Sulfonamides* are derived from the sulfonic acids. Thus, benzene-sulfonic acid C_6 $H_5\cdot$ $SO_2\cdot$ OH becomes benzene-sulfonamide C_6 $H_5\cdot$ $SO_2\cdot$ NH_2. See also **Sulfonamide Drugs**.

Amides may be made in a number of ways. Prominent among them is the acylation of amines. The agents commonly used are, in order of reactivity, the acid halides, acid anhydrides, and esters. Such reactions are:

$$R'COCl + HNR_2 \longrightarrow R'C(=O)NR_2 + HCl$$

$$R'C(=O)OC(=O)R' + HNR_2 \longrightarrow R'C(=O)NR_2 + R'COOH$$

$$R'C(=O)OR'' + HNR_2 \longrightarrow R'C(=O)NR_2 + R''OH$$

The hydrolysis of nitriles also yields amides:

$$RCN + H_2O \xrightarrow{OH} RCONH_2$$

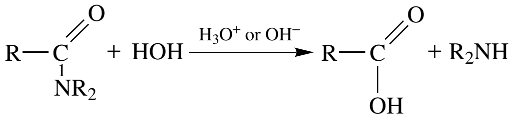
Amides are resonance compounds, having an ionic structure for one form:

$$R{-}C(=O)NR_2 \qquad R{-}C(-O^-) : N^+R_2$$

Evidence for the ionic form is provided by the fact that the carbon-nitrogen bond (1.38 Å) is shorter than a normal C−N bond (1.47 Å) and the carbon-oxygen bond (1.28 Å) is longer than a typical carbonyl bond (1.21 Å). That is, the carbon-nitrogen bond is neither a real C−N single bond nor a C−N double bond.

The amides are sharp-melting crystalline compounds and make good derivatives for any of the acyl classes of compounds, i.e., esters, acids, acid halides, anhydrides, and lactones.

Amides undergo hydrolysis upon refluxing in H_2O. The reaction is catalyzed by acid or alkali.



$$R{-}C(=O)NR_2 + HOH \xrightarrow{H_3O^+ \text{ or } OH^-} R{-}C(=O)OH + R_2NH$$

Primary amides may be dehydrated to yield nitriles.

$$R{-}CONH_2 + C_6H_5SO_2Cl \xrightarrow[70^\circ]{\text{pyridine}} R{-}CN + C_6H_5SO_3H + HCl$$

The reaction is run in pyridine solutions.

Primary and secondary amides of the type $RCONH_2$ and RCONHR react with nitrous acid in the same way as do the corresponding primary and secondary amines.

$$RCONH_2 + HONO \longrightarrow RCOOH + N_2 + HOH$$

$$RCONHR + HONO \longrightarrow RCON(NO)R + HOH$$

When diamides having their amide groups not far apart are heated, they lose ammonia to yield imides. See also **Imides**.

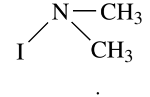
AMINATION. The process of introducing the amino group ($-NH_2$) into an organic compound is termed *amination*. An example is the reduction of aniline, $C_6H_5\cdot NH_2$, from nitrobenzene, $C_6H_5\cdot NO_2$. The reduction may be accomplished with iron and HCl. Only about 2% of the calculated amount of acid (to produce H_2 by reaction with iron) is required because of the fact that H_2 O plus iron in the presence of ferrous chloride solution (ferrous and chloride ions) functions as the primary reducing agent. Such groups as nitroso (−NO), hydroxylamine (−NH · NH−), and azo (−N:N−) also yield amines by reduction. Amination also may be effected by the use of NH_3, in a process sometimes referred to as *ammonolysis*. An example is the production of aniline from chlorobenzene:

$$C_6H_5Cl + NH_3 \longrightarrow C_6H_5\cdot NH_2 + HCl$$

The reaction proceeds only under high pressure. In the ammonolysis of benzenoid sulfonic acid derivatives, an oxidizing agent is added to prevent the formation of soluble reduction products, such as $NaNH_4$ SO_4, which commonly form. Oxygen-function compounds also may be subjected to ammonolysis: (1) methanol plus aluminum phosphate catalyst yields mono-, di-, and trimethylamines; (2) β-naphthol plus sodium ammonium sulfite catalyst (Bucherer reaction) yields β-naphthylamine; (3) ethylene oxide yields mono-, di-, and triethanolamines; (4) glucose plus nickel catalyst yields glucamine; and (5) cyclohexanone plus nickel catalyst yields cyclohexylamine.

AMINES. An amine is a derivative of NH_3 in which there is a replacement for one or more of the H atoms of NH_3 by an alkyl group, such as $-CH_3$ (methyl) or $-C_2H_5$ (ethyl); or by an aryl group, such as $-C_6H_5$ (phenyl) or $-C_{10}H_7$ (naphthyl). Mixed amines contain at least one alkyl and one aryl group as exemplified by methylphenylamine $CH_3\cdot N(H)\cdot C_6H_5$. When one, two, and three H atoms are thus replaced, the resulting amines are known as *primary, secondary*, and *tertiary*, respectively. Thus, methylamine, CH_3NH_2, is a primary amine; dimethylamine, $(CH_3)_2NH$, is a secondary amine; and trimethylamine, $(CH_3)_3N$, is a tertiary amine. Secondary amines sometimes are called *imines*; tertiary amines, *nitriles*.

Quaternary amines consist of four alkyl or aryl groups attached to an N atom and, therefore, may be considered substituted ammonium bases. Commonly, they are referred to in the trade as quaternary ammonium compounds. An example is tetramethyl ammonium iodide.



The amines and quaternary ammonium compounds, exhibiting such great versatility for forming substitution products, are very important starting and intermediate materials for industrial organic syntheses, both on a small scale for preparing rare compounds for use in research and on a tonnage basis for the preparation of resins, plastics, and other synthetics. Very important industrially are the ethanolamines which are excellent absorbents for certain materials. See also **Ethanolamines**. Hexamethylene tetramine is a high-tonnage product used in plastics production. See also **Hexamine**. Phenylamine (aniline), although not as important industrially as it was some years ago, still is produced in quantity. Melamine is produced on a large scale and is the base for a series of important resins. See also **Melamine**. There are numerous amines and quaternary ammonium compounds that are not well known because of their importance as intermediates rather than as final products. Examples along these lines may include acetonitrile and acrylonitrile. See also **Acrylonitrile**.

Primary amines react (1) with nitrous acid, yielding (a) with alkylamine, nitrogen gas plus alcohol, (b) with warm arylamine, nitrogen gas plus phenol (the amino-group of primary amines is displaced by the hydroxyl group to form alcohol or phenol), (c) with cold arylamine, diazonium compounds, (2) with acetyl chloride or benzoyl chloride, yielding substituted amides, thus, ethylamine plus acetyl chloride forms *N*-ethylacetamide, $C_2H_5NHOCCH_3$, (3) with benzene-sulfonyl chloride, $C_6H_5SO_2Cl$, yielding substituted benzene sulfonamides, thus, ethylamine forms *N*-ethylbenzenesulfonamide, $C_6H_5SO_2{-}NHC_2H_5$, soluble in sodium hydroxide, (4) with chloroform, $CHCl_3$ with a base, yielding isocyanides (5) with HNO_3 (concentrated), yielding nitra-mines, thus, ethylamine reacts to form ethylnitramine, $C_2H_5{-}NHNO_2$.

Secondary amines react (1) with nitrous acid, yielding nitrosamines, yellow oily liquids, volatile in steam, soluble in ether. The secondary amine may be recovered by heating the nitrosamine with concentrated HCl, or hydrazines may be formed by reduction of the nitrosamines, e.g., methylaniline from methylphenylnitrosamine, $CH_3(C_6H_5)NNO$, reduction yielding unsymmetrical methylphenylhydrazine, $CH_3(C_6H_5)NHNH_2$, (2) with acetyl or benzoyl chloride, yielding substituted amides, thus, diethylamine plus acetyl chloride to form *N*, *N*-diethylacetamide $(C_2H_5){-}NOCCH_3$, (3) with benzene sulfonyl chloride, yielding substituted benzene sulfonamides, thus, diethylamine reacts to form *N*, *N*-diethylbenzenesulfonamide, $C_6H_5SO_2N(C_2H_5)_2$, insoluble in NaOH.

Tertiary amines do not react with nitrous acid, acetyl chloride, benzoyl chloride, benzenesulfonyl chloride, but react with alkyl halides to form quaternary ammonium halides, which are converted by silver hydroxide to quaternary ammonium hydroxides. Quaternary ammonium hydroxides upon heating yield (1) tertiary amine plus alcohol (or, for higher members, olefin plus water). Tertiary amines may also be formed (2) by alkylation of secondary amines, e.g., by dimethyl sulfate, (3) from amino acids by living organisms, e.g., decomposition of fish in the case of trimethylamine.

AMINO ACIDS. The scores of proteins which make up about one-half of the dry weight of the human body and that are so vital to life functions are made up of a number of amino acids in various combinations and configurations. The manner in which the complex protein structures are assembled from amino acids is described in the entry on Protein. For some users of this book, it may be helpful to scan that portion of the protein entry that deals with the chemical nature of proteins prior to considering the details of this immediate entry on amino acids.

Although the proteins resulting from amino acid assembly are ultimately among the most important chemicals in the animal body (as well as plants), the so-called infrastructure of the proteins is dependent upon the amino acid building blocks. Although there are many hundreds of amino acids, only about 20 of these are considered very important to living processes, of which six to ten are classified as essential. Another three or four may be classified as quasi-essential, and ten to twelve may be categorized as nonessential. As more is learned about the fundamentals, protein chemistry, the scientific importance attached to specific amino acids varies. Usually, as the learning process continues, the findings tend to increase the importance of specific amino acids. Actually, the words *essential* and *nonessential* are not very good choices for naming categories of amino acids. Generally, those amino acids that the human body cannot synthesize at all or at a rate commensurate with its needs are called *essential amino acids* (EAA). In other words, for the growth and maintenance of a normal healthy body, it is essential that these amino acids be ingested as part of the diet and in the necessary quantities. To illustrate some of the indefinite character of amino acid nomenclature, some authorities classify histidine as an essential amino acid; others do not. The fact is that histidine is essential for the normal growth of the human infant, but to date it is not regarded as essential for adults. By extension of the preceding explanation, the term nonessential is taken to mean those amino acids that are really synthesized in the body and hence need not be present in food intake. This classification of amino acids, although amenable to change as the results of new findings, has been quite convenient in planning the dietary needs of people as well as of farm animals, pets, and also in terms of those plants that are of economic importance. The classification has been particularly helpful in planning the specific nutritional content of food substances involved in various aid and related programs for the people in needy and underdeveloped areas of the world.

Food Fortification with Amino Acids. In a report of the World Health Organization, the following observation has been made: “To determine the quality of a protein, two factors have to be distinguished, namely, the proportion of essential to nonessential amino acids and, secondly, the relative amounts of the essential amino acids... The best pattern of essential amino acids for meeting human requirements was that found in whole egg protein or human milk, and comparisons of protein quality should be made by reference to the essential amino acid patterns of either of these two proteins.” The ratio of each essential amino acid to the total sum is given for hen’s egg and human and cow’s milk in Table 1.

In the human body, tyrosine and cysteine can be formed from phenylalanine and methionine, respectively. The reverse transformations do not occur. Human infants have an ability to synthesize arginine and histidine in their bodies, but the speed of the process is slow compared with requirements.

Several essential amino acids have been shown to be the limiting factor of nutrition in plant proteins. In advanced countries, the ratio of vegetable proteins to animal proteins in foods is 1.4:1. In underdeveloped nations, the ratio is 3.5:1, which means that people in underdeveloped areas depend upon vegetable proteins. Among vegetable staple foods, wheat easily can be fortified. It is used as flour all over the world. L-Lysine hydrochloride (0.2%) is added to the flour. Wheat bread fortified with lysine is used in several areas of the world; in Japan it is supplied as a school ration.

The situation of fortification in rice is somewhat more complex. Before cooking, rice must be washed (polished) with water. In some countries, the cooking water is allowed to boil over or is discarded. This significant loss of fortified amino acids must be considered. L-Lysine hydrochloride (0.2%) and L-threonine (0.1%) are shaped like rice grain with other nutrients and enveloped in a film. The added materials must hold the initial shape and not dissolve out during boiling, but be easily freed of their coating in the digestive organs.

The amino acids are arranged in accordance with essentiality in Table 2. Each of the four amino acids at the start of the table are all limiting factors of various vegetable proteins. Chick feed usually is supplemented with fish meal, but where the latter is in limited supply, soybean meals are substituted. The demand for DL-methionine, limiting amino acid in soybean meals, is now increasing. When seed meals, such as corn and sorghum, are used as feeds for chickens or pigs, L-lysine hydrochloride must be added for fortification. Lysine production is increasing upward to the level of methionine.

TABLE 1. REPRESENTATIVE ESSENTIAL AMINO ACID PATTERNS *A/E RATIO (MILLIGRAMS PER GRAM OF TOTAL ESSENTIAL AMINO ACIDS)

	Hen’s egg (Whole)	Human milk	Cow’s milk
Total “aromatic” amino acids	195	226	197
Phenylalanine	(114)	(114)	(97)
Tyrosine	(81)	(112)	(100)
Leucine	172	184	196
Valine	141	147	137
Isoleucine	129	132	127
Lysine	125	128	155
Total “S”	107	87	65
Cystine	(46)	(43)	(17)
Methionine	(61)	(44)	(48)
Threonine	99	99	91
Tryptophan	31	34	28

Source: World Health Organization; FAO Nutrition Meeting Report Series, No. 37, Geneva, 1965.

* A/E Ratio equals ten times percentage of single essential amino acid to the total essential amino acids contained.

TABLE 2. IMPORTANT NATURAL AMINO ACIDS AND PRODUCTION

Amino acid	World annual production, tons	Present mode of manufacture	Characteristics
		ESSENTIAL AMINO ACIDS	
DL-Methionine	10^4	Synthesis from acrolein and mercaptan	First limiting amino acid for soybean
L-Lysine. HCl	10^3	Fermentation (AM)*	First limiting amino acid for cereals
L-Threonine	10	Fermentation (AM)	Second limiting amino acid for rice
L-Tryptophan	10	Synthesis from acrylonitrile and resolution	Second limiting amino acid for corn
L-Phenylalanine	10	Synthesis from phenyl-acetaldehyde and resolution	
L-Valine	10	Fermentation (AM)	Rich in plant protein
L-Leucine	10	Extraction from protein	
L-Isoleucine	10	Fermentation (WS)**	Deficient in some cases
		QUASI-ESSENTIAL AMINO ACIDS	
L-Arginine. HCl	10^2	Synthesis from *L*-ornithine Fermentation (AM)	
L-Histidine. HCl	10	Extraction from protein	Essential to human infants
L-Tyrosine	10	Enzymation of phenol and Serine	Limited substitute for phenylalanine
L-Cysteine L-Cystine	10	Extraction from human hair	Limited substitute for methionine
		NONESSENTIAL AMINO ACIDS	
L-Glutamic acid	10^5	Fermentation (WS) Synthesis from acrylonitrile and resolution	MSG, taste enhancer
Glycine	10^3	Synthesis from formaldehyde	Sweetener
DL-Alanine	10^2	Synthesis from acetaldehyde	
L-Aspartic acid	10^2	Enzymation of fumaric acid	Hygienic drug
L-Glutamine	10^2	Fermentation (WS)	Anti-gastroduodenal ulcer drug
L-Serine	<10	Synthesis from glycolonitrile and resolution	Rich in raw silk
L-Proline	<10	Fermentation (AM)	
L-Hydroxyproline	<10	Extraction from gelatin	Rich in gelatin
L-Asparagine	<10	Synthesis from L-aspartic acid	Neurotropic metabolic regulator
L-Alanine	<10	Enzymation of L-aspartic acid	Rich in degummed white silk
L-Dihydroxy-phenylalanine	10^2	Synthesis from piperonal, vanillin, or acrylonitrile and resolution	Specific drug for Parkinson's disease
L-Citrulline	<10	Fermentation (AM)	Ammonia detoxicant
L-Ornithine	<10	Fermentation (AM)	

*AM, artificial mutant;
**WS, wild strain. MSG, monosodium glutamate.

Early Research and Isolation of Amino Acids. Because of such rapid studies made within the past few decades in biochemistry and nutrition, these sciences still have a challenging aura about them. But, it is interesting to note that the first two natural amino acids were isolated by Braconnot in 1820. As shown by Table 3, these two compounds were glycine and leucine. Bopp isolated tyrosine from casein in 1849. Additional amino acids were isolated during the 1880s, but the real thrust into research in this field commenced in the very late 1800s and early 1900s with the work of Emden, Fischer, Mörner, and Hopkins and Cole. It is interesting to observe that Emil Fischer (1852–1919), German chemist and pioneer in the fields of purines and polypeptides, isolated three of these important compounds, namely, proline from gelatin in 1901, valine from casein in 1901, and hydroxyproline from gelatin in 1902. As an understanding of the role of amino acids in protein formation and of the function of proteins in nutrition progressed, the pathway was prepared for further isolation of amino acids. For example, in 1907, a combined committee representing the American Society of Biological Chemists and the American Physiological Society, proposed a formal classification of proteins into three major categories: (1) simple proteins, (2) conjugated proteins, and (3) derived proteins. The last classification embraces all denatured proteins and hydrolytic products or protein breakdown and no longer is considered as a general class.

Very approximate annual worldwide production of amino acids, their current method of preparation (not exclusive), and general characteristics are given in Table 2.

The *isoelectric point* is very important in the preparation and separation of amino acids and proteins. Protein solubility varies markedly with pH and is at a minimum at the isoelectric point. By raising the salt concentration and adjusting pH to the isoelectric point, it is often possible to obtain a precipitate considerably enriched in the desired protein and to crystallize it from a heterogenous mixture.

Chemical Nature of Amino Acids

In a very general way, an amino acid is any organic acid that incorporates one or more amino groups. This definition includes a multitude of substances of most diverse structure. There are seemingly limitless related compounds of differing molecular size and constitution which incorporate varying kinds and numbers of functional groups. Most extensive study has centered on the relatively small group of alpha-amino acids that are combined in amide linkage to form proteins. With few exceptions, these compounds possess the general structure $NH_2{-}CHRCO_2{-}H$, where the amino group occupies a position on the carbon atom alpha to that of the carboxyl group, and where the side chain R may be of diverse composition and structure.

Few products of natural origin are as versatile in their behavior and properties as are the amino acids, and few have such a variety of biological duties to perform. Among their general characteristics would be included:

(a) Water-soluble and amphoteric electrolytes, with the ability to form acid salts and basic salts and thus act as buffers over at least two ranges of pH (hydrogen ion concentration).
(b) Dipolar ions of high electric moment with a considerable capacity to increase the dielectric constant of the medium in which they are dissolved.
(c) Compounds with reactive groups capable of a wide range of chemical alterations leading readily to a large variety of degradation, synthetic, and transformation products, such as esters, amides, amines, anhydrides, polymers, polypeptides, diketopiperazines, hydroxy acids, halogenated acids, keto acids, acylated acids, mercaptans, shorter-or longer-chained acids, and pyrrolidine and piperidine ring forms.
(d) Indispensable components of the diet of all animals including humans.
(e) Participants in crucial metabolic reactions on which life depends, and substrates for a variety of specific enzymes in vitro.
(f) Binders of metals of many kinds.

Optical Properties. With the exception of glycine ($NH_2{-}CH_2{-}CO_2{-}H$) and amino-malonic acid [$NH_2{-}CH(CO_2H)_2$], all α-amino acids which are classifiable according to the general formula previously given exist in at least two different optically isometric forms. The optical isomers of a given amino acid possess identical empirical and structural formulas, and are indistinguishable from each other on the basis of their chemical and physical properties, with the singular exception of their effect on plane

TABLE 3. FIRST ISOLATION OF AMINO ACIDS

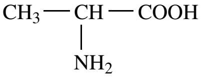
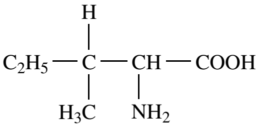
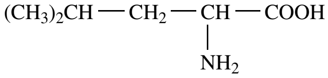
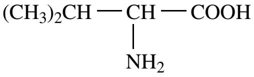
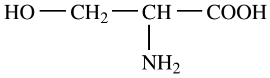
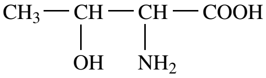
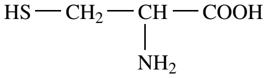
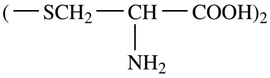
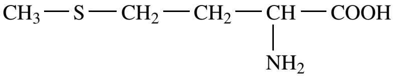
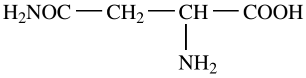
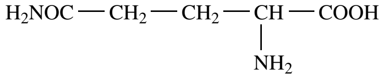
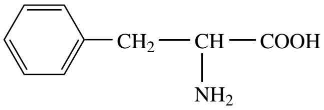
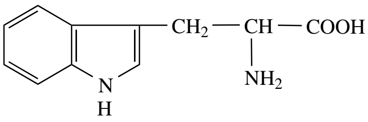
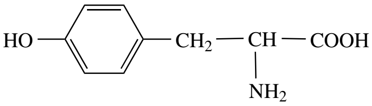
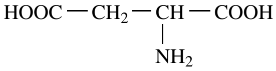
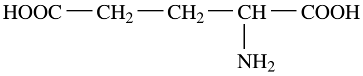
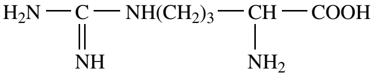
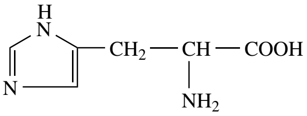
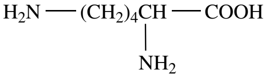
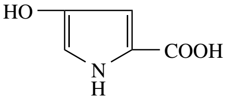
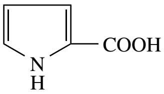
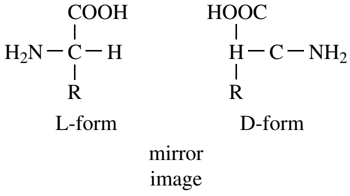
Abbreviation	Name and formula	First isolation and (Source)	Isoelectric point
NEUTRAL AMINO ACIDS-ALIPHATIC TYPE			
Ala	Alanine  $CH_3-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1879 by Schutzenberger 1888 by Weyl (silk fibroin)	6.0
Gly	Glycine NH_2-CH_2-COOH	1820 by Braconnot (gelatin)	6.0
Ile	Isoleucine  $C_2H_5-\overset{H}{\underset{H_3C}{C}}-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1904 by Ehrlich (fibrin)	6.0
Leu	Leucine  $(CH_3)_2CH-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1820 by Braconnot (muscle fiber; wool)	6.0
Val	Valine  $(CH_3)_2CH-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1901 by Fischer (casein)	6.0
NEUTRAL AMINO ACIDS—HYDROXY TYPE			
Ser	Serine  $HO-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1865 by Cramer (sericine)	5.7
Thr	Threonine  $CH_3-\underset{OH}{\underset{\vert}{CH}}-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1925 by Gortner and Hoffman 1925 by Schryver and uston oat protein)	6.2
NEUTRAL AMINO ACIDS—SULFUR-CONTAINING TYPE			
Cys	Cysteine  $HS-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	———	5.1
Cys Cys	Cystine  $(-SCH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH)_2$	1899 by Mörner (horn) 1899 by Emden	4.6
Met	Methionine  $CH_3-S-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1922 by Mueller (casein)	5.7
NEUTRAL AMINO ACIDS—AMIDE TYPE			
Asn	Asparagine  $H_2NOC-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1932 by Damodaran (edestin)	5.4
Gln	Glutamine  $H_2NOC-CH_2-CH_2-\underset{NH_2}{\underset{\vert}{CH}}-COOH$	1932 by Damodaran, Jaaback, and Chibnall (gliadin)	5.7
Phe	Phenylalanine 	1881 by Schulze and Barbieri (lupine seedings)	5.5

TABLE 3. (*continued*)

Abbreviation	Name and Formula	First Isolation and (Source)	Isoelectric Point
Trp	Tryptophan 	1902 by Hopkins and Cole (casein)	5.9
Tyr	Tyrosine 	1849 by Bopp (casein)	5.7
	ACIDIC AMINO ACIDS		
Asp	Aspartic Acid  $HOOC-CH_2-\underset{NH_2}{CH}-COOH$	1868 by Ritthausen (conglutin; legumin)	2.8
Glu	Glumatic Acid  $HOOC-CH_2-CH_2-\underset{NH_2}{CH}-COOH$	1866 by Ritthausen (gluten-fibrin)	3.2
	BASIC AMINO ACIDS		
Arg	Arginine  $H_2N-\underset{NH}{C}-NH(CH_2)_3-\underset{NH_2}{CH}-COOH$	1895 by Hedin (horn)	11.2
His	Histidine 	1896 by Kossel (sturine) 1896 by Hedin (various protein ydrolysates)	7.6
Lys	Lysine  $H_2N-(CH_2)_4\underset{NH_2}{CH}-COOH$	1889 by Dreschel (casein)	9.7
	IMINO ACIDS		
Hyp	Hydroxyproline 	1902 by Fischer (gelatin)	5.8
Pro	Proline 	1901 by Fischer (casein)	6.3

polarized light. This may be illustrated with the two optically active forms as shown by



One form (L-form) exhibits the ability to rotate the plane of polarization of plane polarized light to the left (levorotatory), whereas the other form (D-form) rotates the plane to the right (dextrorotatory). Although the direction of optical rotation exhibited by these optically active forms is different, the magnitude of their respective rotations is the same. If equal amounts of *dextro* and *levo* forms are admixed, the optical effect of each isomer is neutralized by the other, and an optically inactive product known as a *racemic modification* or *racemate* is secured.

The ability of the alanine molecule, for example, to exist in two stereo-isomeric forms can be attributed to the fact that the α-carbon atom of this compound is attached to four different groups which may vary in their three-dimensional spatial arrangement. Compounds of this type do not possess complete symmetry when viewed from a purely geometrical standpoint and hence are generally referred to as *asymmetric*. As a consequence of this molecular asymmetry, the four covalent bonds of an asymmetric carbon atom can be aligned in a manner such that a regular tetrahedron is formed by the straight lines connecting their ends. Hence, two different tetrahedral arrangements of the groups about the asymmetric carbon atom can be devised so that these structures relate to one another as an object relates to its mirror image, or as the right hand relates to the left hand. Molecules of this type are endowed with the property of optical activity and, together with their nonsuperimposable mirror images, are generally referred to as *enantiomorphs, enantiomers, antimers*, or *optical antipodes*.

Classification. In accordance with the structure of the R-group, the amino acids of primary importance can be classified into eight groups. Additional amino acids composing protein are not included in this classification, because they occur infrequently. See Table 4.

Normally, amino acids exist as dipolar ions. $RCH(NH_3^+)COO^-$, in a neutral state, where both amino and carboxyl groups are ionized. The dipolar form, $RCH(NH_2)COOH$ may be considered, but the dipolar form predominates for the usual monoamino monocarboxylic acid and it is estimated that these forms occur 10^5 to 10^6 times more frequently than the non-polar forms. Amino acids decompose thermally at what might be considered a relatively high temperature (200–300°C). The compounds are practically insoluble in organic solvents, have low vapor pressure, and do not exhibit a precisely defined melting point.

The ionic states of a simple α-amino acid are given by

$$\underset{\text{(Cationic form; acidic)}}{RCH(NH_3^+)COOH} \quad \underset{+H^+}{\overset{-H+(K_1)}{\rightleftharpoons}}$$

$$\underset{\text{(Dipolar form; neutral)}}{RCH(NH_3^+)COO^-} \quad \underset{+H^+}{\overset{-H+(K_2)}{\rightleftharpoons}} \quad \underset{\text{(Anionic form; basic)}}{RCH(NH_2)COO^-}$$

In accordance with the change of the ionic state, dissociation constants are

$$K_1(COOH) = \frac{[H^+][RCH(NH_3^+)COO^-]}{[RCH(NH_3^+)COOH]}$$

$$K_2(NH_3^+) = \frac{[H^+][RCH(NH_2)COO^-]}{[RCH(NH_3^+)COO^-]}$$

In as much as $pK = -\log K$, the values for glycine are $pK_1 = 2.34$ and $pK_2 = 9.60$ (in aqueous solution at 25°C). The homologous amino acids indicate similar values. The pH at which acidic ionization balances basic ionization is termed the *isoelectric point* (pH_I), (corresponding to

$$[RCH(NH_3^+)COOH] = [RCH(NH_2)COO^-]$$

TABLE 4. STRUCTURAL CLASSIFICATION OF AMINO ACIDS

	NEUTRAL AMINO ACIDS	
Aliphatic-type	*Hydroxy-type*	*Sulfur-containing*
Glycine	Serine	Cysteine
Alanine	Threonine	Cystine
Valine		Methionine
Leucine		
Isoleucine		
Amide-type	*Aromatic-type*	
Asparagine	Phenylalanine	
Glutamine	Tryptophan	
	Tyrosine	
	ACIDIC AMINO ACIDS	
Aspartic acid		
Glutamic acid		
	BASIC AMINO ACIDS	
Histidine		
Lysine		
Arginine		
	IMINO ACIDS	
Proline		
Hydroxyproline		

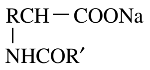
Thus, from these formulas, the pH_I is

$$pH_I = \tfrac{1}{2}(pK_1 + pK_2)$$

Formation of Salts. Amino acids have certain characteristics of both organic bases and organic acids because they are amphoteric. As amines, the amino acids form stable salts, such as hydrochlorides or aromatic sulfonic acid salts. These are used as selective precipitants of certain amino acids. As organic acids, the amino acids form complex salts with heavy metals, the less soluble salt being used for amino acid separation.

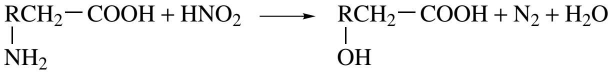
Esters. When heated with the equivalent amount of a strong acid, usually hydrochloric acid in absolute alcohol, amino acids form esters. These are obtained as hydrochlorides.

Acylation. In alkaline solution, amino acids react with acid chlorides or acid anhydrides to form acyl compounds of the type



$$\underset{\displaystyle NHCOR'}{RCH}\!-\!COONa$$

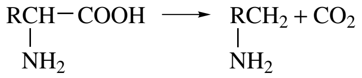
Van Slyke Reaction (Deamination). With excess nitrous acid, -amino acids react to form-hydroxyl acids on a quantitative basis. Nitrogen gas is generated.



$$\underset{\displaystyle NH_2}{RCH_2}\!-\!COOH + HNO_2 \longrightarrow \underset{\displaystyle OH}{RCH_2}\!-\!COOH + N_2 + H_2O$$

The reaction is completed within five minutes at room temperature. Thus, measurement of the volume of nitrogen generated can be used in amino acid determinations.

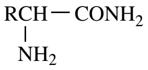
Decarboxylation. When heated with inert solvents, such as kerosene, amino acids form amines



$$\underset{\displaystyle NH_2}{RCH}\!-\!COOH \longrightarrow \underset{\displaystyle NH_2}{RCH_2} + CO_2$$

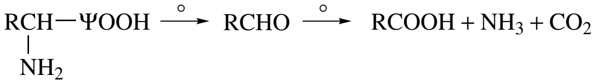
Decarboxylative enzymes may react specifically with amino acids having free polar groups at the ω position. Cadaverine can be produced from lysine, histamine from histidine, and tyramine from tyrosine.

Formation of Amides. When condensed with ammonia or amines, amino acid esters form acid amides:



$$\underset{\displaystyle NH_2}{RCH}\!-\!CONH_2$$

Oxidation. Oxidizing agents easily decompose α-amino acids, forming the corresponding fatty acid with one less carbon number:



$$\underset{\displaystyle NH_2}{RCH}\!-\!\Psi OOH \xrightarrow{\circ} RCHO \xrightarrow{\circ} RCOOH + NH_3 + CO_2$$

Ninhydrin Reaction. A neutral solution of an amino acid will react with ninhydrin (triketohydrindene hydrate) by heating to cause oxidative decarboxylation. The central carbonyl of the triketone is reduced to an alcohol. This alcohol further reacts with ammonia formed from the amino acid and causes a red-purplish color. Since the reaction is quantitative, measurement of the optical density of the color produced is an indication of amino acid concentration. Imino acids, such as hydroxyproline and proline, develop a yellow color in the same type of reaction.

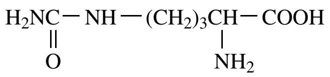
Maillard Reaction. In amino acids, the amino group tends to form condensation products with aldehydes. This reaction is regarded as the cause of the browning reaction when an amino acid and a sugar coexist. A characteristic flavor, useful in food preparations, is evolved along with the color in this reaction.

Ion-exchange Separations. Because amino acids are amphoteric, they behave as acids or bases, depending upon the pH of the solution. This makes it possible to adsorb amino acids dissolved in water on either a strong-acid cation exchange resin; or a strong-base anion exchange resin. The affinity varies with the amino acid and the solution pH. Ion-exchange resins are widely used in amino acid separations.

Production of Amino Acids. There are three means available for making (or separating) amino acids in large quantity lots: (1) extraction from natural protein; (2) fermentation; and (3) chemical synthesis. During the early investigations of amino acids, the first method was widely used and still applies to four amino acids. See Table 3.

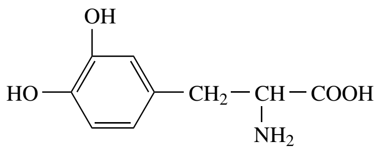
L-Leucine is easily extracted in quantity from almost any type of vegetable protein hydrolyzates. Cystine is extracted from the human-hair hydrolyzate. L-Histidine is obtainable from the blood of animals, but future yields may stem from fermentation inasmuch as some artificial mutants of bacteria have been discovered. Gelatin is the prime source of L-hydroxyproline.

Natural amino acids, normally not contained in proteins, but which are effective in medicine, include citrulline, ornithine, and dihydroxyphenylalanine. These are not listed in Tables 2 and 3. Citrulline (Cit) with an isoelectric point of 5.9 was isolated by Koga in 1914; by Odake in 1914; and by Wada in 1930. It has the formula

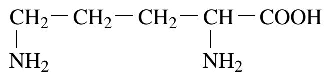


$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{H_2NC}}-\mathrm{NH}-(\mathrm{CH_2})_3\underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{CH}}-\mathrm{COOH}$$

Dihydroxyphenylalanine (Dopa) with an isoelectric point of 5.5 was isolated by Torquati in 1913; and by Guggenheim in 1913. It has the formula



Ornithine (Orn) with an isoelectric point of 9.7 was isolated by Riesser in 1906 from arginine. It has the formula



$$\underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{CH_2}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{CH}}-\mathrm{COOH}$$

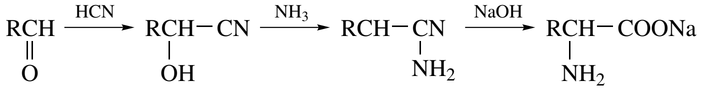
Fermentation Methods. Numerous microorganisms can synthesize the amino acids required to support their life from a simple carbon source and an inorganic nitrogen source, such as ammonium or nitrate salts, or nitrogen gas.

Japanese microbiologists, in 1956, first succeeded in developing industrial production of L-glutamic acid by a microbiological process. As of the present, nearly all common amino acids can be produced on a low cost industrial scale by fermentation. From microbiological studies, it has been ascertained that some microbial stains isolated from natural sources serve to excrete and accumulate a large amount of a particular amino acid in the cultural broth under carefully controlled conditions. The production of glutamic acid is produced by adding a selected bacterial strain and culturing aerobically for one to two days in a chemically defined medium which contains carbon sources, such as sugar or acetate, and nitrogen sources, such as ammonium salts. About 50% (wt) of the carbon sources can be converted to glutamate.

Genetic techniques have been used to improve the ability of microorganisms to accumulate amino acids. Several amino acids are manufactured from their direct precursors by the use of microbially produced enzymes. For example, bacterial L-aspartate β-carboxylase is used for the production of L-alanine from L-aspartic acid.

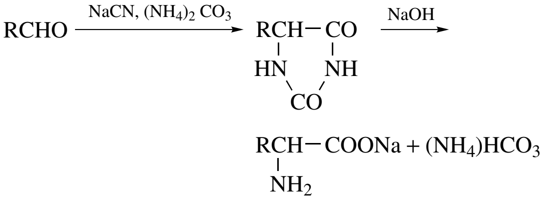
In isolating the amino acids from the fermentation broth, chromatographic separations using ion-exchange resins are the most important commercial method. Precipitation with compounds which yield insoluble salts with amino acids are also used. Purification is possible by crystallization through careful adjustment of the isoelectric point, at which point the amino acid is least soluble.

There are several laboratory-size methods for synthesizing amino acids, but few of these have been scaled up for industrial production. Glycine and DL-alanine are made by the Strecker synthesis, commencing with formaldehyde and acetaldehyde, respectively. In the Strecker synthesis, aldehydes react with hydrogen cyanide and excess ammonia to give amino nitriles which, in turn, are converted into α-amino acids upon hydrolysis.



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{RCH}} \xrightarrow{\mathrm{HCN}} \underset{\substack{| \\ \mathrm{OH}}}{\mathrm{RCH}}-\mathrm{CN} \xrightarrow{\mathrm{NH_3}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{CN} \xrightarrow{\mathrm{NaOH}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{COONa}$$

The Hydantoin Process. Hydantoins are produced by reacting aldehydes with sodium cyanide and ammonium carbonate. Upon hydrolysis, α-amino acids will be yielded



$$\mathrm{RCHO} \xrightarrow{\mathrm{NaCN,\ (NH_4)_2\,CO_3}} \mathrm{RCH{-}CO,\ HN,\ NH,\ CO} \xrightarrow{\mathrm{NaOH}} \underset{\substack{| \\ \mathrm{NH_2}}}{\mathrm{RCH}}-\mathrm{COONa} + (\mathrm{NH_4})\mathrm{HCO_3}$$

The production of α-amino acids by chemical synthesis yields a mixture of DL forms. The D-form of glutamic acid has no flavor-enhancing properties and thus requires transformation into the optically active form insofar as monosodium glutamate is concerned. The three methods for separating the optical isomers are: (1) preferential inoculation method; (2) the diastereoisomer method; and (3) the acylase method.

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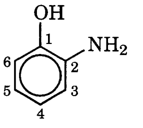
AMINO RESINS. A family of resins resulting from an addition reaction between formaldehyde and compounds, such as aniline, ethylene urea, dicyandiamide, melamine, sulfonamide, and urea. The resins are thermosetting and have been used for many years in such products as textile-treating agents, laminating coatings, wet-strength paper coatings, and wood adhesives. The urea and melamine compounds are the most widely used. Both of these basic resins are water white (transparent). However, the resins readily accept pigments and opacifying agents. The addition of cellulose filler can be used to reduce light transmission. Where color is unimportant, various materials are added to the melamine resin compounds, including macerated fabric, glass fiber, and wood flour. Wood flour frequently is added to the urea resins to yield a low cost industrial material.

Advantages claimed for amino resins include: (1) good electrical insulation characteristics, (2) no transfer of tastes and odors to foods, (3) self-extinguishing burning characteristics, (4) resistance to attack by oils, greases, weak alkalis and acids, and organic solvents, (5) abrasion resistance, (6) good rigidity, (7) easy fabrication by economical molding procedures, (8) excellent resistance to deformation under load, (9) good subzero characteristics with no tendency to become brittle, and (10) marked hardness.

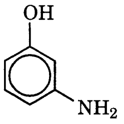
Amino resins are fabricated principally by transfer and compression molding. Injection molding and extrusion are used on a limited scale. Urea resins are not recommended for outdoor exposure. The resins show rather high mold shrinkage and some shrinkage with age. The melamines are superior to the ureas insofar as resistance to heat and boiling water, acids, and alkalis is concerned.

Some of the hundreds of applications for amino resins include: closures for glass, metal, and plastic containers; electrical wiring devices; appliance knobs, dials, handles, and push buttons; lamp shades and lighting diffusers; organ and piano keys; dinnerware; food service trays; food-mixer housings; switch parts; decorative buttons; meter blocks; aircraft ignition parts; heavy duty switch gear; connectors; and terminal strips. Not all of the urea or melamine amino resins are suited to all of the foregoing uses. Because of the large number of fillers and additives available, the overall range of use of this family of resins is large.

AMINOPHENOLS. Aminophenols and their derivatives are of commercial importance, both in their own right and as intermediates in the photographic, pharmaceutical, and chemical dye industries. They are amphoteric and can behave either as weak acids or weak bases, but the basic character usually predominates. 3-Aminophenol (**2**) is fairly stable in air unlike 2-aminophenol (**1**) and 4-aminophenol (**3**) which easily undergo oxidation to colored products. The former are generally converted to their acid salts, whereas 4-aminophenol is usually formulated with low concentrations of antioxidants which act as inhibitors against undesired oxidation.



(**1**)



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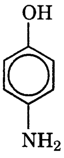


(**3**)

Physical Properties

The simple aminophenols exist in three isomeric forms depending on the relative positions of the amino and hydroxyl groups around the benzene ring. At room temperature they are solid crystalline compounds. In the past the commercial-grade materials were usually impure and colored because of contamination with oxidation products, but now virtually colorless, high purity commercial grades are available. General properties are listed in Table 1.

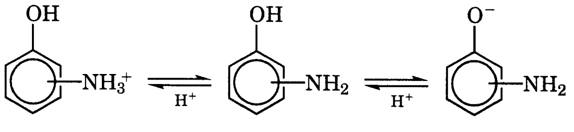
2-Aminophenol. This compound forms white orthorhombic, bipyramidal needles when crystallized from water or benzene, which readily become yellow-brown on exposure to air and light.

3-Aminophenol. This is the most stable of the isomers under atmospheric conditions. It forms white prisms when crystallized from water or toluene.

4-Aminophenol. This compound forms white plates when crystallized from water. The base is difficult to maintain in the free state and deteriorates rapidly under the influence of air to pink-purple oxidation products.

Chemical Properties

The chemical properties and reactions of the aminophenols and their derivatives are to be found in detail in many standard chemical texts. The acidity of the hydroxyl function is depressed by the presence of an amino group on the benzene ring; this phenomenon is most pronounced with 4-aminophenol. The amino group behaves as a weak base, giving salts with both mineral and organic acids. The aminophenols are true ampholytes, with no zwitterion structure; hence they exist either as neutral molecules (**4**), or as ammonium cations (**5**), or phenolate ions (**6**), depending on the pH value of the solution.



(**5**) (**4**) (**6**)

The aminophenols are chemically reactive, undergoing reactions involving both the aromatic amino group and the phenolic hydroxyl moiety, as well as substitution on the benzene ring. Oxidation leads to the formation of highly colored polymeric quinoid structures. 2-Aminophenol undergoes a variety of cyclization reactions. Important reactions include alkylation, acylation, diazonium salt formation, cyclization reactions, condensation reactions, and reactions of the benzene ring.

Manufacture and Processing

Aminophenols are either made by reduction of nitrophenols or by substitution. Reduction is accomplished with iron or hydrogen in the presence of a catalyst. Catalytic reduction is the method of choice for the production of 2- and 3-aminophenol. Electrolytic reduction is also under industrial consideration and substitution reactions provide the major source of 3-aminophenol.

Purification

Contaminants and by-products which are usually present in 2- and 4-aminophenol made by catalytic reduction can be reduced or even removed completely by a variety of procedures. These include treatment with 2-propanol, with aliphatic, cycloaliphatic, or aromatic ketones, with aromatic amines, with toluene or low mass alkyl acetates, or with phosphoric acid, hydroxyacetic acid, hydroxypropionic acid, or citric acid. In addition, purity may be enhanced by extraction with methylene chloride, chloroform, or nitrobenzene. Another method employed is the treatment of aqueous solutions of aminophenols with activated carbon.

Economic Aspects

Production figures for the aminophenols are scarce, the compounds usually being classified along with many other aniline derivatives. Most production of the technical grade materials (95% purity) occurs on-site, as they are chiefly used as intermediate reactants in continuous chemical syntheses. World production of the fine chemicals (99% purity) is probably no more than a few hundred metric tons yearly.

Storage

Under atmospheric conditions, 3-aminophenol is the most stable of the three isomers. Both 2- and 4-aminophenol are unstable; they darken on exposure to air and light and should be stored in brown glass containers, preferably in an atmosphere of nitrogen. The use of activated iron oxide

TABLE 1. GENERAL PROPERTIES OF AMINOPHENOLS

Property	2-Aminophenol	3-Aminophenol	4-Aminophenol
alternative names	2-hydroxyaniline 2-amino-1-hydroxybenzene	3-hydroxyaniline 3-amino-1-hydroxybenzene	4-hydroxyaniline 4-hydroxy-1-aminobenzene
molecular formula	C_6H_7NO	C_6H_7NO	C_6H_7NO
molecular weight	109.13	109.13	109.13
melting point, °C	174	122–123	189–190[a]
boiling point, °C			
1.47 kPa	153[b]	164	174
101.3 kPa			284
ΔH_f, kJ/mol[c]	-191.0 ± 0.9	-194.1 ± 1.0	-190.6 ± 0.9[d]

[a] Decomposes.

[b] Sublimes. To convert kPa to mm Hg, multiply by 7.5.

[c] In the crystalline state. To convert kJ to kcal, divide by 4.184.

[d] −179.1 is also noted.

in a separate cellophane bag inside the storage container, or the addition of stannous chloride or sodium bisulfite inhibits the discoloration of aminophenols. The salts, especially the hydrochlorides, are more resistant to oxidation and should be used where possible.

Health and Safety Factors

In general, aminophenols are irritants. Their toxic hazard rating is slight to moderate and their acute oral toxicities in the rat (LD_{50}) are quoted as 1.3 g/kg, 1.0 g/kg, and 0.375 g/kg body weight for the 2-, 3-, and 4-isomer, respectively.

4-Aminophenol is a selective nephrotoxic agent and interrupts proximal tubular function.

Teratogenic effects have been noted with 2- and 4-aminophenol in the hamster, but 3-aminophenol was without effect in the hamster and rat.

Obviously, care should be taken in handling these compounds, with the wearing of chemical-resistant gloves and safety goggles; prolonged exposure should be avoided.

The addition of slaked lime and the initiation of polymerization reactions with H_2O_2 and ferric or stannous salts are techniques employed to remove aminophenols from wastewaters.

Uses

The aminophenols are versatile intermediates and their principal use is as synthesis precursors; their products are represented among virtually every class of stain and dye.

Derivatives

The derivatives of the aminophenols have important uses in both the photographic and pharmaceutical industries. They are also extensively employed as precursors and intermediates in the synthesis of more complicated molecules, especially those used in the staining and dye industry. All of the major classes of dyes have representatives that incorporate substituted aminophenols; those compounds produced commercially as dye intermediates have been reviewed. Details of the more commonly encountered derivatives of the aminophenols can be found in standard organic chemistry texts.

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Additional Reading

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AMMINES. Dry ammonia gas reacts with dehydrated salts of some of the metals to form solid ammines. Ammines, upon warming, evolve ammonia, sometimes with final decomposition of the salt itself, in a manner analogous to the decomposition of certain hydrates. The ammines of chromium(III)(Cr^{3+}), cobalt(III), platinum(IV), and other metals have been studied in detail. Two series of ammines are shown in Fig. 1 the first is one in which the neutral ammonia group is replaced step by step by the negative nitro group ($NO_2{}^-$), the second is one in which the neutral ammonia group is replaced, step by step, by the neutral H_2O group.

The neutral group of the complex may be replaced step by step by the following negative groups: Cl^-, Br^-, I^-, F^-, OH^-, $NO_2{}^-$, $NO_3{}^-$, CN^-, CNS^-, $SO_4{}^{2-}$, $CO_3{}^{2-}$, $C_2O_4{}^{2-}$; or by the following neutral groups: H_2O, NO, NO_2, SO_2, S, N_2H_4, H_2NOH, CO, C_2, H_5OH, C_6H_6. All neutral groups are of substances capable of independent existence.

In the ammines, trivalent metals, such as cobalt(III) and chromium(III) and iron(III), possess a coordination number of 6, this number being the sum of the unit replacements on the metal in the complex ion. Since a regular octahedron has six corners equidistant from the center, it is assumed that the metal occupies the center and each of the six replacing groups occupies a corner of a regular octahedron. Support for this assumption is offered by the x-ray examination of these ammines. When there is only one of the six groups replaced by a second group, as in $[Co(NH_3)_5(NO_2)]Cl_2$, and in $[Cr(NH_3)_5(H_2O)]X_3$ the octahedral placement of groups supplies only one form, but when two of the six groups are replaced by a second group, as in $[Co(NH_3)_4(NO_2)_2]Cl$, and in $[Cr(NH_3)_4(H_2O)_2]X_3$, two different octahedral corner arrangements are possible depending upon whether the two replacing groups are adjacent (cis-form) or opposite (trans-form). Two substances differing in physical properties and corresponding to these two forms are known. Further, when three divalent groups, e.g., $3C_2O_4{}^2A$ are present in the complex, two arrangements—not identical but mirror-images of each other—are possible. Two optically active substances are known in such cases corresponding to these two stereo-isomeric forms.

$[Co(NH_3)_6]Cl_3$
410

$[Co(NH_3)_5(NO_2)]Cl_2$
240

$[Co(NH_3)_4(NO_2)_2]Cl$
95

$[Co(NH_3)_3(NO_2)_3]$
1.5

$K[Co(NH_3)_2(NO_2)_4]$
95

$K_2[Co(NH_3)(NO_2)_5]$
240

$K_2[Co(NO_3)_6]$
420

(**a**)

$[Cr(NH_3)_6]X_3$
$[Cr(NH_3)_5H_2O)]X_3$
$[Cr(NH_3)_4H_2O_2]X_3$
$[Cr(NH_3)_3(H_2O)_3]X_3$
$[Cr(NH_3)_2(H_2O)_4]X_3$

X = unit anion

(**b**)

Fig. 1. Two series of ammines: (**a**) Square bracket contains the ion. The equivalent electrical conductivity is shown below each compound. The number of neutral groups, e.g., (NH_3), on metal, e.g., Co, is varied from 6 to 0. (**b**) The number of neutral groups is constant, but the groups are varied

Six is the ordinary coordination number for metallic ammines and similar complexes. Additional examples are $K_2[Pt(NH_3)_2(CN)_4]$, $[Ni(NH_3)_6]Cl_2$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN_6)]$, $K_2[Fe(CN)_5(NO)]$, $K_2[SiF_6]$, $[Ca(NH_3)_6]Cl_2$. But, for the elements boron, carbon, and nitrogen four is the coordination number, e.g., $[BH_4]Cl$, CH_4, $NH_4]Cl$, and in these substances the groups are assumed to occupy the corners of a regular tetrahedron; in $[K_4Mo(CN)_8]$ and $[Ba(NH_3)_8]Cl_2$ the coordination number is eight, and the groups are assumed to occupy the corners of a cube.

AMMONIA. [CAS: 7664-41-7]. Known since ancient times, ammonia, NH_3 has been commercially important for well over 100 years and has become the second largest chemical in terms of tonnage and the first chemical in value of production. The first practical plant of any magnitude was built in 1913. Worldwide production of NH_3 as of the early 1980s is estimated at 100 million metric tons per year or more, with the United States accounting for about 14% of the total production. A little over three-fourths of ammonia production in the United States is used for fertilizer, of which nearly one-third is for direct application. An estimated 5.5% of ammonia production is based in the manufacture of fibers and plastics intermediates.

Properties. At standard temperature and pressure, NH_3 is a colorless gas with a penetrating, pungent-sharp odor in small concentrations which, in heavy concentrations, produces a smothering sensation when inhaled. Formula weight is 17.03, mp −77.7°C, bp −33.35°C, and sp gr 0.817 (at −79°C) and 0.617 (at 15°C). Ammonia is very soluble in water, a saturated solution containing approximately 45% NH_3 (weight) at the freezing temperature of the solution and about 30% (weight) at standard conditions. Ammonia dissolved in water forms a strongly alkaline solution of ammonium hydroxide, NH_4OH. The univalent radical NH_4^+ behaves in many respects like K^+ and Na^+ in vigorously reacting with acids to form salts. Ammonia is an excellent nonaqueous electrolytic solvent, its ionizing power approaching that of water. Ammonia burns with a greenish-yellow flame.

Ammonia derives its name from sal ammoniac, NH_4Cl, the latter material having been produced at the Temple of Jupiter Ammon (Libya) by distilling camel dung. During the Middle Ages, NH_3 was referred to as the spirits of hartshorn because it was produced by heating the hoofs and horns of oxen. The composition of ammonia was first established by Claude Louis Berthollet (France, ca. 1777). The first significant commercial source of NH_3 (during the 1880s) was its production as a byproduct in the making of manufactured gas through the destructive distillation of coal. See also **Coal Tar and Derivatives**.

Nitrogen fixation is a term assigned to the process of converting nitrogen in the air to nitrogen compounds. Although some bacteria in soil are capable of this process, N_2 as an ingredient of fertilizer is required for soils that are depleted by crop production. The production of synthetic NH_3 is the most important industrial nitrogen-fixation process. See also **Fertilizer**.

Synthesis of Ammonia

The first breakthrough in the large-scale synthesis of ammonia resulted from the work of Fritz Haber (Germany, 1913), who found that ammonia could be produced by the direct combination of two elements, nitrogen and hydrogen, ($N_2 + 3H_2 \rightleftharpoons 2NH_3$) in the presence of a catalyst (iron oxide with small quantities of cerium and chromium) at a relatively high temperature (550°C) and under a pressure of about 200 atmospheres, representing difficult processing conditions for that era. Largely because of the urgent requirements for ammonia in the manufacture of explosives during World War I, the process was adapted for industrial-quality production by Karl Bosch, who received one-half of the 1931 Nobel Prize for chemistry in recognition of these achievements. Thereafter, many improved ammonia-synthesis systems, based on the Haber-Bosch process, were commercialized, using various operating conditions and synthesis-loop designs.

The principal features of an NH_3 synthesis process system are the converter designs, operating conditions, method of product recovery, and type of re-circulation equipment. Most current systems operate at or above the pressure used in the original Haber-Bosch process. Converter designs have either a single continuous catalyst bed, which may or may not have heat-exchange cooling for controlling reaction heat, or several catalyst beds with provision for temperature control between the beds.

Claude Process. The original Claude process was one of the first systems to use a high operating pressure (1000 atmospheres), achieving 40% conversion without recycling. This system used multiple converters in a series-parallel arrangement. The present Claude process[1] operates at 340–650 atmospheres, using a single converter with continuous catalyst-charged tubes externally cooled to remove the heat of reaction. Approximate hydrogen conversion is 30–34 mole percent per pass. The pressure is increased gradually to compensate for catalyst aging and loss in activity. Product recovery is by simple condensation in a water-cooled condenser. Nonreacted gas is recycled by compressor.

Casale Process. This is another high-pressure conversion system, using synthesis pressures of 450–600 atmospheres, which also permits hydrogen conversions in the 30 mole percent range. As in the Claude process, the high pressure allows NH_3 to be recovered from the converter effluent by water cooling. The Casale converter uses a single catalyst bed with internal heat-exchange surfaces. Reaction rate and temperature rise across the catalyst are controlled by the internal exchanger and retaining 2–3 mole percent NH_3 in the converter feed. An ejector is used to remove nonreacted gas. This eliminates the need for a mechanical recycle compressor, but requires high feed-gas pressures to supply the energy required for the ejector.

Low-Pressure Processes. Several systems use low synthesis pressures with hydrogen conversion below 30 mole percent and product recovery by water and refrigeration.

Synthesis-Gas-Production Processes. These processes were improved and developed as a result of changes in feedstock availability and economics. Before World War II, most NH_3 plants obtained H_2 by reacting coal or coke with steam in the water-gas process. A small number of plants used water electrolysis or coke-oven byproduct hydrogen. The subsequent low-cost availability of natural gas brought about steam-hydrocarbon reforming as the major source of H_2 for the NH_3 synthesis gas.

Partial oxidation processes to produce H_2 from natural gas and liquid hydrocarbons were also developed after World War II and accounted for 15% of the synthetic NH_3 capacity by 1962. The steam-hydrocarbon reforming process[2] was developed in 1930. In this process, methane was mixed with an excess of steam at atmospheric pressure, and the mixture reformed inside nickel-catalyst-filled alloy furnace tubes. The heat of reaction was supplied by externally heating the catalyst-filled tubes to about 871°C. Since the late 1950s, improvements in the tubular-reforming technology and metallurgy have brought about the utilization of high-pressure (>24 atmospheres) reforming, which cut synthesis-gas-compression costs and increased heat recovery. The first pressure reformer[3] was built in 1953. In addition, the higher pressures allowed improvements in the efficiency of synthesis-gas-purification systems. High-pressure steam-reforming technology also has been extended to cover heavier hydrocarbon gases, including propane, butane, reformer gases, and streams containing a high amount of olefins. In 1962, a process[4] for reforming straight-run liquid distillates (naphthas) was commercialized. This process is based on the use of an alkali oxide-promoted nickel catalyst[5] which permits reforming of desulfurized naphthas at low (~3.5:1) steam-to-carbon ratios, without significant carbon deposition problems.

Noncatalytic partial oxidation processes designed to produce H_2 from a wide range of hydrocarbon liquids, including heavy fuel oils, crudes, naphthas, coal tar, and pulverized bituminous coal, were commercialized in 1954[6] and 1956.[7] In both these processes, the hydrocarbon feed is oxidized and reformed in a refractory-lined pressure vessel. The required oxygen usually is supplied by an air separation plant from which nitrogen also is used as feed for the synthesis gas. The main differences between the two processes are in the reactor design, feeding method, burner design, and carbon and heat recovery. The partial oxidation processes and the steam-naphtha reforming process are favored in areas with short supplies of natural gas.

The source of nitrogen for the synthesis gas has always been air, either supplied directly from a liquid-air separation plant or by burning a small amount of the hydrogen with air in the H_2 gas. The need for air separation plants has been eliminated in modern ammonia plants by use of secondary reforming, where residual methane from the primary reformer is adiabatically reformed with sufficient air to produce a 3:1 mole ratio hydrogen-nitrogen synthesis gas.

Most ammonia plants built since the early 1960s are in the 600–1500 short tons/day (540–1350 metric tons/day) range and are based on new integrated designs that have cut the cost of ammonia manufacture in half. The plants of the early 1960s, in fact, have reached the best combination in terms of plant overall efficiency and cost by combining all the separate units (e.g., synthesis-gas preparation, purification, and ammonia synthesis) in one single train. High-pressure reforming has reduced the synthesis-gas compression load and front end plant equipment size. This compactness in design has also led to increased plant size at reduced investment and operating costs.

Use of Multistage Centrifugal Compressors. One of the major factors contributing to the improved economics of ammonia plants is the application of multistage centrifugal compressors, which have replaced the reciprocating compressors traditionally used in the synthesis feed and recycle service. A single centrifugal compressor can do the job of several banks of reciprocating compressors, thus reducing equipment cost, floor space, supporting foundations, and maintenance.

The use of multistage centrifugal compressors was made possible by redesigning the synthesis loop to operate at low pressures (150–240 atmospheres) and by increasing plant capacity to above the compressor's minimum-flow restriction in order to obtain a reasonable compressor efficiency. (Most synthesis loops using reciprocating compressors had been operating at intermediate pressures of 300–350 atmospheres.) Centrifugal compressors capable of developing pressures up to 340 atmospheres already

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[1] Developed by Grande Pariosse and L'Air Liquide.

[2] Originally developed by Standard Oil Company of New Jersey.

[3] Built by M.W. Kellogg for Shell Chemical Corp. (Ventra, California).

[4] W. Kellogg and Imperial Chemical Industries.

[5] Developed by M.W. Kellogg.

[6] Texaco partial oxidation process.

[7] Shell gasification process.

are being offered and used in some large-capacity (1000 short tons/day; 900 metric tons/day) plants, where the increasing compressor horsepower is partially offset by reduction of the refrigeration horsepower requirement.

An operating ammonia plant using the aforementioned improvements is shown schematically in Fig. 1. This plant[8] has a capacity of 1000 short tons/day (900 metric tons/day) and uses natural gas as feedstock. The plant can be divided into the following integrated-process sections: (a) synthesis-gas preparation; (b) synthesis-gas purification; and (c) compression and ammonia synthesis. A typical (Kellogg designed) ammonia plant is shown in Fig. 2.

Synthesis Gas Preparation. The desulfurized natural gas mixed with steam is fed to the primary reformer, where it is reacted with steam in nickel-catalyst-filled tubes to produce a major percentage of the hydrogen required. The principal reactions taking place are[9]

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (1)$$

$$\Delta H_{298} = 49.3\text{kcal/mole}$$

$$CO + H_2OsCO_2 + H_2 \qquad (2)$$

$$\Delta H_{298} = -9.8\text{kcal/mole}$$

Reaction (1) is the principal reforming reaction, and reaction (2) is the water-gas shift reaction. The net reactions are highly endothermic. The partially reformed gas leaves the primary reformer containing approximately 10% methane, on a mole dry-gas basis, at 27–34 atmospheres and up to 816°C. The required heat of reaction is supplied by natural-gas-fired arch burners, which are designed to also burn purge and flash gases from the synthesis section. Waste heat from the primary reformer flue gas is recovered by generating high-pressure superheated steam, which along with waste-heat process boilers and an appended auxiliary boiler assure a steam system that is always in balance, while providing high-pressure steam to compressor turbine drivers and low-pressure steam to pump drivers. Further waste heat is recovered by preheating the natural-gas-steam feed mixture, steam-air for secondary reforming, and fuel.

The primary reforming step is followed by conversion of the residual methane to hydrogen and carbon oxides over a bed of high-temperature chrome and nickel catalysts in the secondary reformer. The secondary reforming step not only achieves a great degree of overall reforming economically possible, but also reduces fuel-gas input and overall reforming costs by shifting part of the required hydrocarbon conversion from the high-cost primary reformer to the lower-cost secondary reformer. It also permits an increase in the residual methane level at the primary effluent, which results in lower operating temperatures, reduced steam requirements, and milder tube-metal conditions.

Process waste-heat boilers then cool the reformed gas to about 371°C while generating high-pressure steam. The cooled gas-stream mixture enters a two-stage shift converter. The purpose of shift conversion is to convert CO to CO_2 and produce an equivalent amount of H_2 by the reaction: $CO + H_2O \rightleftharpoons CO_2 + H_2$. Since the reaction rate in the shift converter is favored by high temperatures, but equilibrium is favored by low temperatures, two conversion stages, each with a different catalyst provide the optimum conditions for maximum CO shift. Gas from the shift converter is the raw synthesis gas, which, after purification, becomes the feed to the NH_3 synthesis section.

Purification of Synthesis Gas. This involves the removal of carbon oxides to prevent poisoning of the NH_3 catalyst. An absorption process is used to remove the bulk of the CO_2, followed by methanation of the residual carbon oxides in the methanator. Modern ammonia plants use a variety of CO_2-removal processes with effective absorbent solutions. The principal absorbent solutions currently in use are hot carbonates and ethanolamines. Other solutions used include methanol, acetone, liquid nitrogen, glycols, and other organic solvents.

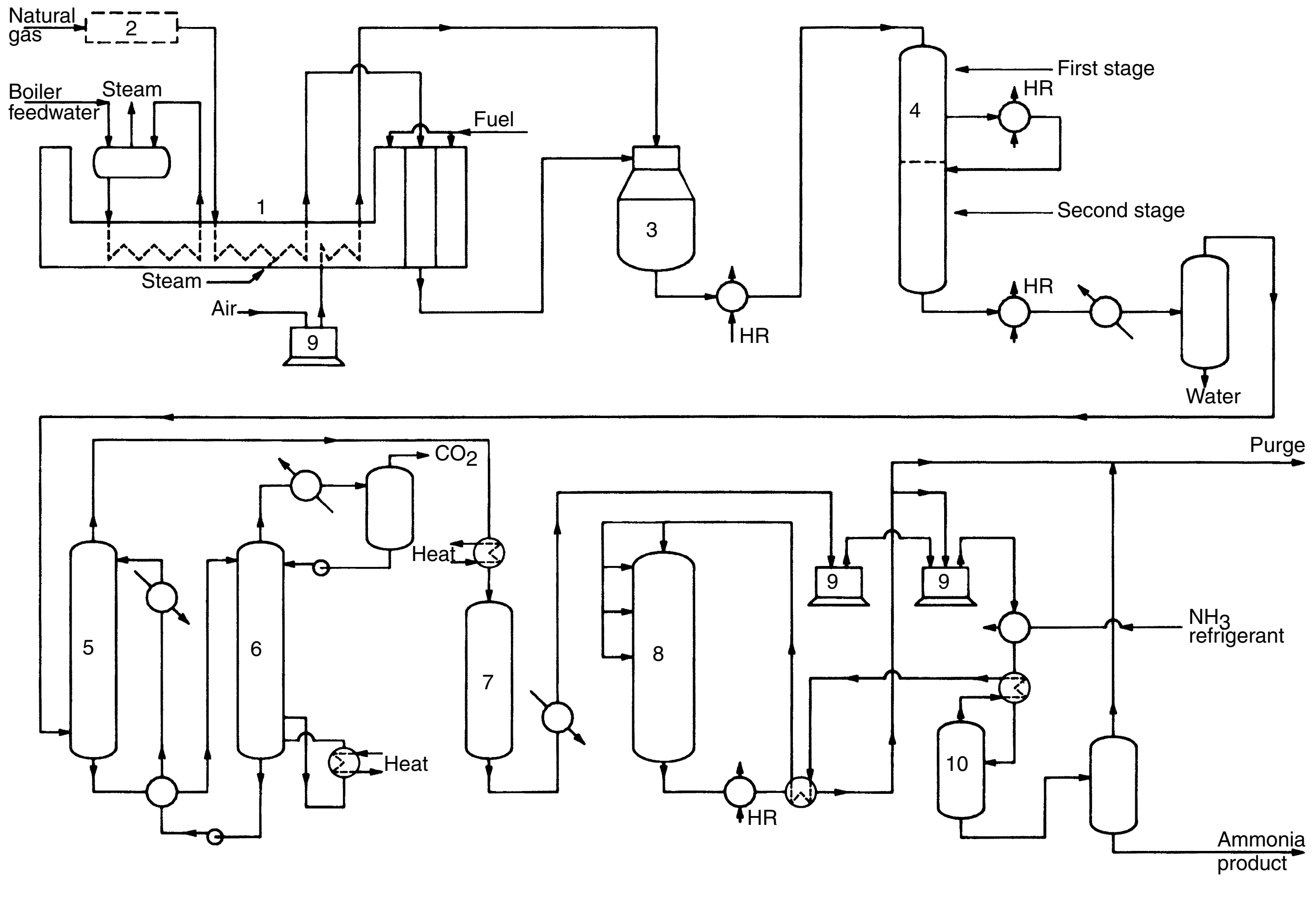

Fig. 1. Ammonia production process: (1) Primary reformer, (2) desulfurization, (3) secondary reformer, (4) CO shift converter (in two stages), (5) CO_2 absorber, (6) CO_2 stripper, (7) methanator, (8) NH_3 converter, (9) compressor, (10) separator. HR=heat recovery. (*M.W. Kellogg*)

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[8] Designed by The M.W. Kellogg Company, Houston, Texas, for which Kellogg received the 1967 Kirkpatrick Chemical Engineering Achievement Award.

[9] Heats of reaction at 198°K (25°C), 1 atmosphere pressure, gaseous substances in ideal state.

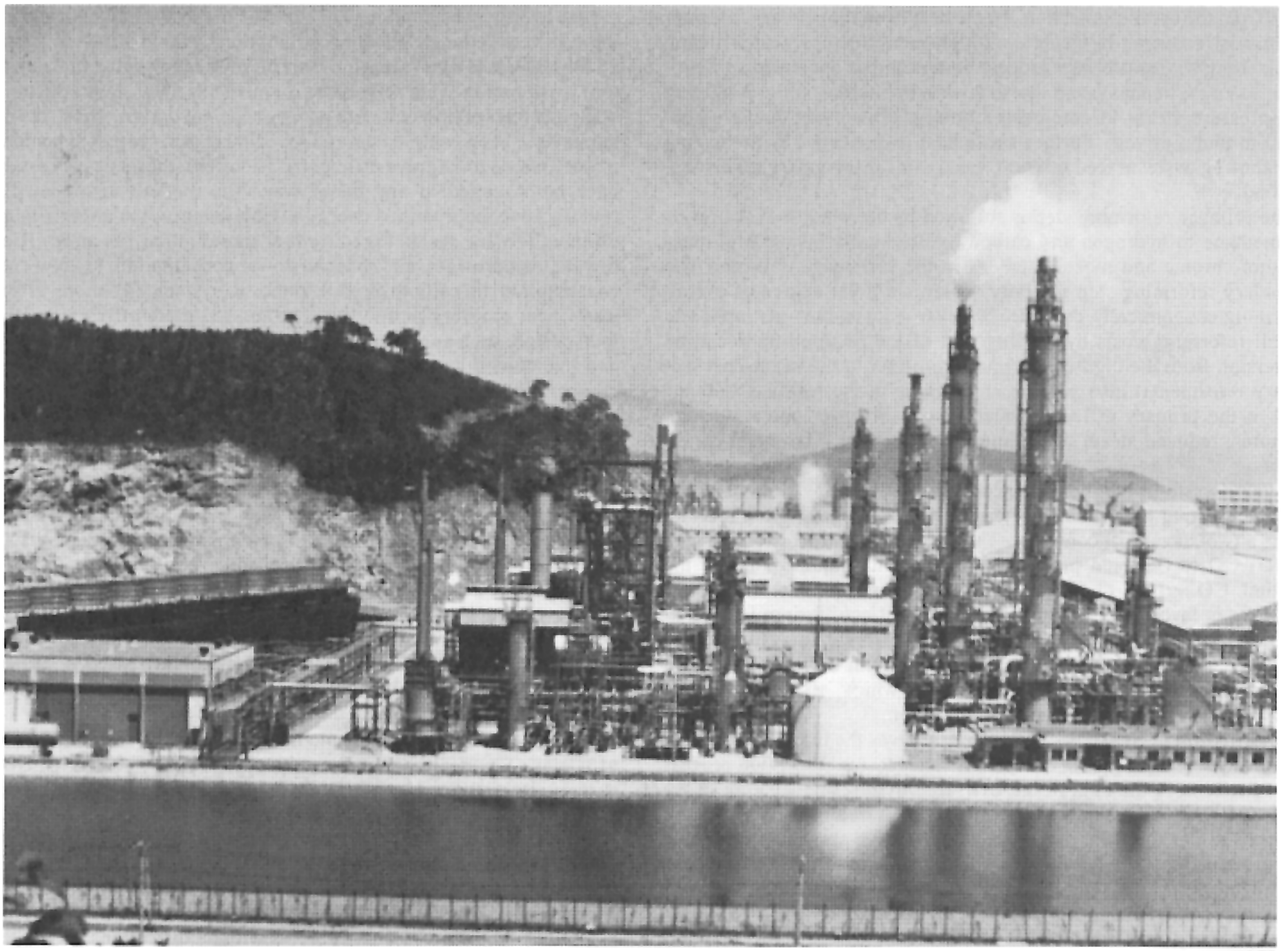

Fig. 2. Two 1000 short tons/day (900 metric tons/day) Kellogg-designed modern ammonia plants. (*M.W. Kellogg*)

The partially purified synthesis gas leaves the CO_2 absorber containing approximately 0.1% CO_2 and 0.5% CO. This gas is preheated at the methanator inlet by heat exchange with the synthesis-gas compressor interstage cooler and the primary-shift converter effluent and reacted over a nickel oxide catalyst bed in the methanator. The methanation reactions are highly exothermic and are equilibrium favored by low temperatures and high pressures.

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

The methanator effluent is cooled by heat exchange with boiler feedwater and cooling water. The synthesis gas leaves the methanator containing less than 10 parts per million (ppm) of carbon oxides.

Compression and Synthesis. The purified synthesis gas, containing H_2 and N_2 in a 3:1 mole ratio and with an inert gas (methane and argon) content of about 1.3 mole percent, is delivered to the suction of the synthesis-gas compressor. Anhydrous ammonia is catalytically synthesized in the converter. The effluent from the converter, after taking off a small purge stream, is recycled for eventual conversion to ammonia. Reaction takes place at approximately 370–482°C. Ammonia liquid, separated from the loop in the separator and from the purge, contains dissolved synthesis gas, which is released when the combined stream is flashed into the letdown drum. The flashed gas is then separated in the letdown drum and combined with the vapors from the purge separator to form a stream of purge fuel gases. Liquid ammonia in the letdown drum still contains some dissolved gases that must be disengaged. This liquid ammonia is let down to the refrigeration system where the dissolved gases are flashed and released to fuel. A centrifugal compressor is used to provide the refrigeration for the ammonia condensing. Ammonia product is withdrawn from the ammonia refrigeration system.

Modern Ammonia Plant. Since the development of the single train ammonia plant in the 1960s, many improvements have been made to reduce energy consumption. The plant of the 1980s has achieved striking results of reducing energy consumption by 20 to 30%—to less than 25 MMBTU(LHV)/ST (million Btus of low heating value fuel per short ton) of ammonia. This achievement represents a constant effort of development in seeking out more energy efficient design. Those developments have been centered around the 1960s basic process scheme with modifications to improve efficiency. Therefore, the basic process steps have not changed in any major way. The modern ammonia plants (after 1980) have incorporated energy-saving features, including: (1) more efficient furnace design to reduce fuel consumption, (2) more efficient drivers, compressors, and reduced power consumption, (3) low energy consumption in carbon dioxide removal system, (4) more efficient waste heat recovery and utilization, and (5) more efficient synthesis loop design, such as make-up gas drying, purge gas hydrogen recovery, and intercooled ammonia converter. The trend toward greater energy conservation is expected to continue.

Future Considerations in Ammonia Production. In addition to continued emphasis on energy efficiency, alternate feedstocks will continue to be a primary area of ammonia technology.

In the past, coal or heavy hydrocarbon feedstock ammonia plants were not economically competitive with plants where the feedstocks were light hydrocarbons (natural gas to naphtha). Because of changing economics, however, plants that can handle heavy hydrocarbon feedstock are now attracting increasing attention. In addition, the continuous development and improvement of partial oxidation processes at higher pressure have allowed reductions in equipment size and cost. Therefore, the alternate feedback ammonia plants based on a partial oxidation process may become economically competitive in the near future.

The ultimate goal of any ammonia process will be the direct fixation of nitrogen by reaction of water with air, $1.5H_2O + 0.5N_2 \rightleftharpoons NH_3 + 0.75O_2$. The theoretical energy requirement of the reaction is about 18 MMBTU/ST of ammonia. This feed energy requirement is the same as a natural gas feed ammonia plant. The major difference is that there is no short supply of water, air, and solar energy. However, the technology required for this route is not expected to be available any time soon. It is believed that, in the near future, ammonia plant designs will be based essentially on the present-day process with modifications to reduce energy consumption.

Additional Reading

Aika, K. and A. Neilsen: *Ammonia, Catalysis and Manufacture*, Springer-Verlag New York, Inc., New York, NY, 1995.

Appl, M.: *Ammonia, Principles and Industrial Practice*, John Wiley & Sons, Inc., New York, NY, 1999.

Staff: *Ammonia Plant Safety & Related Facilities,* Vol. 39, American Institute of Chemical Engineers, New York, NY, 1999.

AMMONIUM CHLORIDE. [CAS: 12125-02-9]. NH_4Cl, formula weight 53.50, white crystalline solid, decomposes at 350°, sublimes at 520°C under controlled conditions, sp gr 1.52. Also known as *sal ammoniac*, the compound is soluble in H_2O and in aqueous solutions of NH_3; slightly soluble in methyl alcohol. Ammonium chloride is a high-tonnage chemical, finding uses as an ingredient of dry cell batteries, as a soldering flux, as a processing ingredient in textile printing and hide tanning, and as a starting material for the manufacture of other ammonium chemicals. The compound can be produced by neutralizing HCl with NH_3 gas or with liquid NH_4OH, evaporating the excess H_2O, followed by drying, crystallizing, and screening operations. The product also can be formed in the gaseous phase by the reacting of hydrogen chloride gas with NH_3. Ammonium chloride generally is not attractive as a source of nitrogen for fertilizers because of the build-up and damaging effects of chloride residuals in the soil. See also **Nitrogen**.

AMMONIUM COMPOUNDS. Several of the principal ammonium compounds are described in separate entries in this volume. See also **Ammonium Chloride**; **Ammonium Nitrate**; **Ammonium Phosphates**; and **Ammonium Sulfate**. The important aspects of several other ammonium compounds are summarized below.

Acetate: Ammonium acetate [CAS: 631-61-8] $NH_4C_2H_3O_2$, white solid, soluble, formed by reaction of ammonia or NH_4OH and acetic acid, reacts upon heating to yield acetamide.

Alum: Ammonium alums are those alums, such as aluminum ammonium sulfate $Al_2(NH_4)_2\ (SO_4)_4 \cdot 24H_2O$, ferric ammonium sulfate $Fe_2(NH_4)_2(SO_4)_4 \cdot 24H_2O$, chromium ammonium sulfate $Cr_2(NH_4)_2\ (SO_4)_4 \cdot 24H_2O$ where ammonium sulfate is crystallized with the heavier metal sulfate.

Benzoate: Ammonium benzoate [CAS: 1863-63-4] $NH_4C_7H_5O_2$, white solid, soluble, formed by reaction of NH_4OH and benzoic acid. Used (1) as a food preservative, (2) in medicine.

Borate: Ammonium borate, [CAS: 11128-98-6] ammonium tetraborate

$$(NH_4)_2B_4O_7 \cdot 4H_2O,$$

white solid, soluble, formed by reaction of NH_4OH and boric acid. Used (1) in fireproofing fabrics, (2) in medicine.

Bromide: Ammonium bromide [CAS: 12124-97-9] NH_4Br white solid, soluble, sublimes at 542°C, formed by reaction of NH_4OH and hydrobromic acid. Used in photography.

Carbonates: Ammonium carbonate, [CAS: 506-87-6] $(NH_4)_2CO_3$, volatile, white solid, soluble, formed by reaction of NH_4OH and CO_2 by crystallization from dilute alcohol, loses NH_3, CO_2, and H_2O at ordinary temperatures, rapidly at 58°C; ammonium hydrogen carbonate, ammonium bicarbonate, ammonium acid carbonate NH_4HCO_3, white solid, soluble, formed by reaction of NH_4OH and excess CO_2. This salt is the important reactant in the ammonia soda process for converting sodium chloride in solution into sodium hydrogen carbonate solid.

Chloroplatinate: Ammonium chloroplatinate [CAS: 16919-58-7] $(NH_4)_2\ PtCl_6$, yellow solid, insoluble, formed by reaction of soluble ammonium salt solutions and chloroplatinic acid. Used in the quantitative determination of ammonium.

Cobaltinitrite: Diammonium sodium cobaltinitrite,

$$(NH_4)_2NaCo(NO_2)_6 \cdot H_2O$$

golden-yellow precipitate, formed by reaction of sodium cobaltinitrite solution in acetic acid with soluble ammonium salt solution. Used in the detection of ammonium.

Cyanate: Ammonium cyanate NH_4CNO, white solid, soluble, formed by fractional crystallization of potassium cyanate and ammonium sulfate (ammonium cyanate is soluble in alcohol), when heated changes into urea.

Dichromate: Ammonium dichromate [CAS: 7789-09-5] $(NH_4)_2Cr_2O_7$, red solid, soluble, upon heating evolves nitrogen gas and leaves a green insoluble residue of chromic oxide.

Fluoride: Ammonium fluoride [CAS: 12125-01-8] NH_4F, white solid, soluble, formed by reaction of NH_4OH and hydrofluoric acid, and then evaporating. Used (1) as an antiseptic in brewing, (2) in etching glass; ammonium hydrogen fluoride, ammonium bifluoride, ammonium acid fluoride NH_4F_2, white solid, soluble.

Iodide: Ammonium iodide [CAS: 12027-06-4] NH_4I, white solid, soluble, formed by reaction of NH_4OH and hydriodic acid, and then evaporating. Used (1) in photography, (2) in medicine.

Linoleate: Ammonium linoleate $NH_4C_{18}H_{31}O_2$. Used (1) as an emulsifying agent, (2) as a detergent.

Nitrite: Ammonium nitrite [CAS: 13446-48-5] NH_4NO_2 when ammonium sulfate or chloride and sodium or potassium nitrite are heated, the mixture behaves like ammonium nitrite in yielding nitrogen gas.

Oxalate: Ammonium oxalate [CAS: 1113-38-8] $(NH_4)_2C_2O_4$, white solid, soluble, formed by reaction of NH_4OH and oxalic acid, and then evaporating. Used as a source of oxalate; ammonium binoxalate $NH_4HC_2O_4 \cdot H_2O$, white solid, soluble.

Perchlorate: Ammonium perchlorate [CAS: 7790-98-9] (NH(4)CLO(4)) is a white crystalline substance. It is a powerful oxidizing material. AP is the oxidizer used in the solid rocket boosters on the space shuttle. It is stable in pure form at ordinary temperature, but decomposes at a temperature of 150 degrees C or above. It becomes an explosive when mixed with finely divided organic materials. AP exhibits the same explosive sensitivity to shock as picric acid (Class A explosive). Sensitivity to shock and friction may be great when contaminated with small amounts of some impurities such as sulfur, powdered metals and carbonaceous materials. AP may explode when involved in fire. *Periodate*: Ammonium periodate NH_4IO_4, white solid, moderately soluble.

Persulfate: Ammonium persulfate [CAS: 7727-54-0] $(NH_4)_2S_2O_8$, white solid, soluble, formed by electrolysis of ammonium sulfate under proper conditions. Used (1) as a bleaching and oxidizing agent, (2) in electroplating, (3) in photography.

Phosphomolybdate: Ammonium phosphomolybdate [CAS: 12026-66-3]

$$(NH_4)_3PO_4 \cdot 12MoO_3$$

(or similar composition), yellow precipitate, soluble in alkalis, formed by excess ammonium molybdate and HNO_3 with soluble phosphate solution. Used as an important test for phosphate (similar product and reaction when arsenate replaces phosphate).

Salicylate: Ammonium salicylate $NH_4C_7H_5O_3$, white solid, soluble, formed by reaction of NH_4OH and salicylic acid, and then evaporating. Used in medicine.

Sulfide: Ammonium sulfide [CAS: 12124-99-1] $(NH_4)_2S$, colorless to yellowish solution, formed by saturation with hydrogen sulfide of one-half of a solution of NH_4OH, and then mixing with the other half of the NH_4OH. Dissolves sulfur to form ammonium polysulfide, yellow solution. Used as a reagent in analytical chemistry; ammonium hydrogen sulfide, ammonium bisulfide, ammonium acid sulfide NH_4HS, colorless to yellowish solution, formed by saturation with H_2S of a solution of NH_4OH.

Tartrate: Ammonium tartrate [CAS: 3164-29-2] $(NH_4)_2C_4H_4O_6$, white solid, moderately soluble, formed by reaction of NH_4OH and tartaric acid, and then evaporating. Used in the textile industry; ammonium hydrogen tartrate, ammonium bitartrate, ammonium acid tartrate $NH_4HC_4H_4O_6$, white solid, slightly soluble, formation sometimes used in detection of ammonium or tartrate.

Thiocyanate: Ammonium thiocyanate, [CAS: 1762-95-4] ammonium sulfocyanide, ammonium rhodanate NH_4CNS, white solid, soluble, absorbs much heat on dissolving with consequent marked lowering of temperature, mp 150°C, formed by boiling ammonium cyanate solution with sulfur, and then evaporating. Used (1) as a reagent for ferric, (2) in making cooling solutions, (3) to make thiourea.

Ammonium compounds liberate NH_3 gas when warmed with NaOH solution.

AMMONIUM HYDROXIDE. [CAS: 1336-21-6]. NH_4OH, formula weight 35.05, exists only in the form of an aqueous solution. The compound is prepared by dissolving NH_3 in H_2O and usually is referred to in industrial trade as aqua ammonia. For industrial procurements, the concentration of NH_3 in solution is normally specified in terms of the specific gravity (degrees Baumé, °Be). Common concentrations are 20 °Be and 26 °Be. The former is equivalent to a sp gr of 0.933, or a concentration of about 17.8% NH_3 in solution; the latter is equivalent to a sp gr of 0.897, or a concentration of about 29.4% NH_3. These figures apply at a temperature of 60°F (15.6°C). Reagent grade NH_4OH usually contains approximately 58% NH_4OH (from 28 to 30% NH_3 in solution).

Ammonium hydroxide is one of the most useful forms in which to react NH_3 (becoming the $NH_4{}^+$ radical in solution) with other materials for the creation of ammonium salts and other ammonium and nitrogen-bearing chemicals. Ammonium hydroxide is a direct ingredient of many products, including saponifiers for oils and fats, deodorants, etching compounds, and cleaning and bleaching compounds. Because aqua ammonia is reasonably inexpensive and a strongly alkaline substance, it finds wide application as a neutralizing agent. See also **Nitrogen**.

AMMONIUM NITRATE. [CAS: 6484-52-2]. NH_4NO_3, formula weight 80.05, colorless crystalline solid, occurs in two forms:

α-NH_4NO_3, tetragonal crystals, stable between −16°C and 32°C, sp gr 1.66.

β-NH_4NO_3, rhombic or monoclinic crystals, stable between 32°C and 84°C, sp gr 1.725.

The melting point generally ascribed to the alpha form is 169.6°C, with decomposition occurring above 210°C. Upon heating, ammonium nitrate yields nitrous oxide (N_2O) gas and can be used as an industrial source of that gas. Ammonium nitrate is soluble in H_2O, slightly soluble in ethyl alcohol, moderately soluble in methyl alcohol, and soluble in acetic acid solutions containing NH_3.

As shown in Fig. 1 in making ammonium nitrate on a large scale, NH_3, vaporized by waste steam from neutralizer, is sparged along with HNO_3 into the neutralizer. A ratio controller automatically maintains the proper proportions of NH_3 and acid. The heat of neutralization evaporates a part of the H_2O and gives a solution of 83% NH_4NO_3. Final evaporation to above 99% for agricultural prills or to approximately 96% for industrial prills is accomplished in a falling-film evaporator located at the top of the prilling tower. The resultant melt flows through spray nozzles and downward through the tower. Air is drawn upward by fans at the top of the tower. The melt is cooled sufficiently to solidify, forming round pellets or prills of the desired range of sizes. The prills are removed from the bottom of the tower and fed to a rotary cooler. Where industrial-type prills are produced, a pre-drier and drier precede the cooler. Fines from the rotary drums are collected in wet cyclones. This solution eventually is returned to the neutralizer. After cooling, the prills are screened to size and the over and undersize particles are sent to a sump and returned to the neutralizer. Intermediate or product-size prills are dusted with a coating material, usually diatomaceous earth, in a rotary coating drum and sent to the bagging operation. The process can be adapted to other types of materials and mixtures of ammonium nitrate and other fertilizer materials. Mixtures include the incorporation of limestone and ammonium phosphates.

Ammonium nitrate is a very high tonnage industrial chemical, finding major applications in explosives and fertilizers, and additional uses in pyrotechnics, freezing mixtures (for obtaining low temperatures), as a slow-burning propellant for missiles (when formulated with other materials, including burning-rate catalysts), as an ingredient in rust inhibitors (especially for vapor-phase corrosion), and as a component of insecticides.

Amatol, an explosive developed by the British, is a mixture of ammonium nitrate and TNT. A special explosive for tree-trunk blasting consists of ammonium nitrate coated with TNT. In strip mining, an explosive consisting of ammonium nitrate and carbon black is used. The explosive ANFO is a mixture of ammonium nitrate and fuel oil. ANFO accounts for about 50% of the commercial explosives used in the United States. Slurry explosives consist of oxidizers (NH_4NO_3 and $NaNO_3$), fuels (coals, oils, aluminum, other carbonaceous materials), sensitizers (TNT, nitrostarch, and smokeless powder), and water mixed with a gelling agent to form a thick, viscous explosive with excellent water-resistant properties. Slurry explosives may be manufactured as cartridged units, or mixed on-site. Although Nobel introduced NH_4NO_3 into his dynamite formulations as early as 1875, the tremendous explosive power of the compound was not realized until the tragic Texas City, Texas disaster of 1947 when a shipload of NH_4NO_3 blew up while in harbor. See also **Explosives**.

As a fertilizer, NH_4NO_3 contains 35% nitrogen. Because of the explosive nature of the compound, precautions in handling are required. This danger can be minimized by introducing calcium carbonate into the mixture, reducing the effective nitrogen content of the product to 26%. In as much as NH_4NO_3 is highly hygroscopic, clay coatings and moisture-proof bags are means used to preclude spoilage in storage and transportation. See also **Fertilizer**; and **Nitrogen**.

AMMONIUM PHOSPHATES. There are two ammonium phosphates, both produced on a very high-tonnage scale; monoammonium phosphate, $NH_4\ H_2PO_4$, white crystals, sp gr 1.803 formula weight 115.04, $N = 12.17\%$; $P_2O_5 = 61.70\%$ diammonium phosphate, $(NH_4)_2HPO_4$, white crystals, sp gr 1.619 formula weight 132.07, $N = 21.22\%$, $P_2O_5 = 53.74\%$

Both compounds are soluble in H_2O; insoluble in alcohol or ether. A third compound, triammonium phosphate $(NH_4)_3PO_4$, does not exist under normal conditions because, upon formation, it immediately decomposes, losing NH_3 and reverting to one of the less alkaline forms.

Large quantities of the ammonium phosphates are used as fertilizers and in fertilizer formulations. The compounds furnish both nitrogen and phosphorus essential to plant growth. The compounds also are used as fire retardants in wood building materials, paper and fabric products, and in matches to prevent afterglow. Solutions of the ammonium phosphates sometimes are air dropped to retard forest fires, serving the double purpose of fire fighting and fertilizing the soil to accelerate new plant growth. The compounds are used in baking powder formulations, as nutrients in

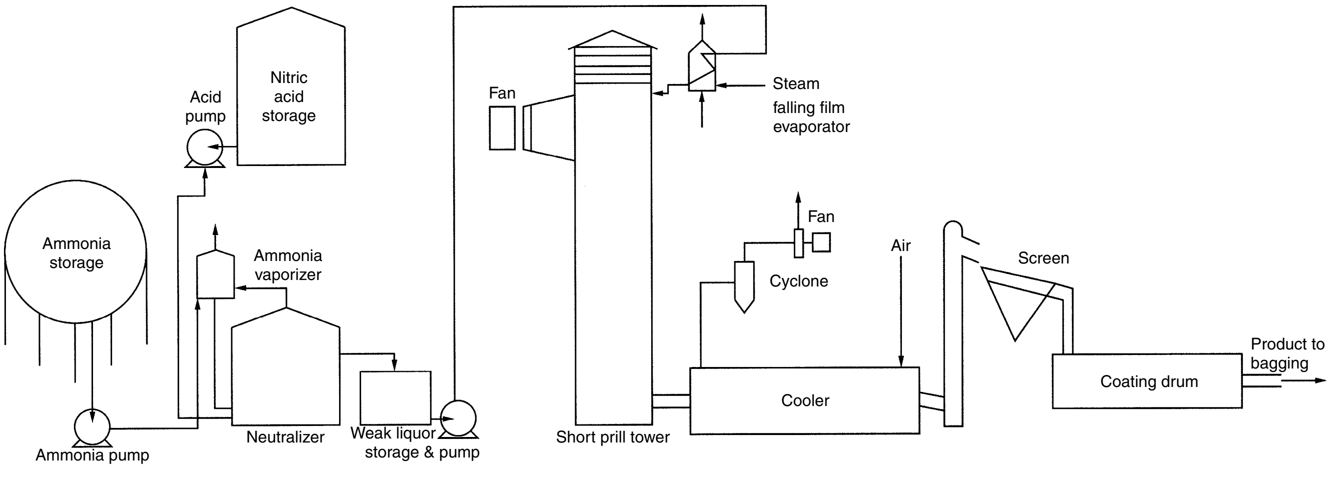

Fig. 1. Process for making ammonium nitrate on a large scale

the production of yeast, as nutritional supplements in animal feeds, for controlling the acidity of dye baths, and as a source of phosphorus in certain kinds of ceramics.

Ammonium phosphates usually are manufactured by neutralizing phosphoric acid with NH_3. Control of the pH (acidity/alkalinity) determines which of the ammonium phosphates will be produced. Pure grades can be easily made by crystallization of solutions obtained from furnace grade phosphoric acid. Fertilizer grades, made from wet-process phosphoric acid, do not crystallize well and usually are prepared by a granulation technique. First, a highly concentrated solution or slurry is obtained by neutralization. Then the slurry is mixed with from 6× to 10× its weight of previously dried material, after which the mixture is dried in a rotary drier. The dry material is then screened to separate the desired product size. Oversize particles are crushed and mixed with fines from the screen operation and then returned to the granulation step where they act as nuclei for the production of further particles. Other ingredients often are added during the granulation of fertilizer grades. The ratio of nitrogen to phosphorus can be altered by the inclusion of ammonium nitrate, ammonium sulfate, or urea. Potassium salts sometimes are added to provide a 3-component fertilizer (N, P, K). A typical fertilizer grade diammonium phosphate will contain 18% N and 46% P_2O_5 (weight). See also **Fertilizer**; and **Nitrogen**.

There has been a trend toward the production of ammonium phosphates in powder form. Concentrated phosphoric acid is neutralized under pressure, and the heat of neutralization is used to remove the water in a spray tower. The powdered product then is collected at the bottom of the tower. Ammonium nitrate/ammonium phosphate combination products can be obtained either by neutralizing mixed nitric acid and phosphoric acid, or by the addition of ammonium phosphate to an ammonium nitrate melt.

AMMONIUM SULFATE. [CAS: 7783-20-2]. $(NH_4)_2SO_4$, formula weight 132.14, colorless crystalline solid, decomposes above 513°C, sp gr 1.769. The compound is soluble in H_2O and insoluble in alcohol. Ammonium sulfate is a high-tonnage industrial chemical, but frequently may be considered a byproduct as well as intended end-product of manufacture. Large quantities of ammonium sulfate result from a variety of industrial neutralization operations required for alleviation of stream pollution by free H_2SO_4. The ammonium sulfate so produced is not always recovered and marketed. A significant commercial source of $(NH_4)_2SO_4$ is its creation as a byproduct in the manufacture of caprolactam, which yields several tons of the compound per ton of caprolactam made. See also **Caprolactam**. Ammonium sulfate also is a byproduct of coke oven operations where the excess NH_3 formed is neutralized with H_2SO_4 to form $(NH_4)_2SO_4$. However, as a major fertilizer and ingredient of fertilizer formulations, additional production is required, largely depending upon the proximity of consumers to byproduct $(NH_4)_2SO_4$ sources. In the Meresburg reaction, natural or byproduct gypsum is reacted with ammonium carbonate:

$$CaSO_4 \cdot 2H_2O + (NH_4)_2CO_3 \longrightarrow CaCO_3 + (NH_4)_2SO_4 + 2\ H_2O$$

The product is stable, free-flowing crystals. As a fertilizer, $(NH_4)_2SO_4$ has the advantage of adding sulfur to the soil as well as nitrogen. By weight, the compound contains 21% N and 24% S. Ammonium sulfate also is used in electric dry cell batteries, as a soldering liquid, as a fire retardant for fabrics and other products, and as a source of certain ammonium chemicals. See also **Fertilizer**; and **Nitrogen**.

AMORPHOUS. As opposed to a crystalline substance which exhibits an orderly structure, the behavior of an amorphous substance is similar to a very viscous, inelastic liquid. Examples of amorphous substances include amber, glass, and pitch. An amorphous material may be regarded as a liquid of great viscosity and high rigidity, with physical properties the same an all directions (may be different for crystalline materials in different directions). Usually, upon heating, an amorphous solid gradually softens and acquires the characteristics of a liquid, but without a definite point of transition from solid to liquid state. In geology, an amorphous mineral lacks a crystalline structure, or has an internal arrangement so irregular that there is no characteristic external form. This does not preclude, however, the existence of any degree of order. The term amorphous is used in connection with amorphous graphite and amorphous peat, among other naturally occurring substances.

AMOSITE. Amosite is a long-fiber gray or greenish asbestiform mineral related to the cummingtonite-grunerite series, and is of economic importance. It occurs within both regional and contact metamorphic rocks in the Republic of South Africa. The name *amosite* is a product of the initial letters of its occurrence at the Asbestos Mines of South Africa. See also **Asbestos**

AMPEROMETER. An instrument for the chemical analysis of electro-reducible or oxidizable ions, molecules, or dissolved gases in solution. Included are the majority of metal ions and many organic substances that contain oxidizable or reducible groups. The range of concentration measurements of which the instrument is capable is from 0.01 to 1,000 ppm. This instrumental method is used for determining free available or total available chlorine, particularly in connection with water-chlorination control. In this application, the range of chlorine concentration is from 0 to 50 ppm. Free iodine also may be determined with an amperometer. The identification of unknown substances is by inference from noting the fixed potential between polarized microelectrode and reference electrode that causes oxidation or reduction of a given composition sought. Where identity is firmly established, the concentration also may be determined because the concentration is proportional to the diffusion-limited current that flows in the electrode circuit. In this latter respect, amperometry is similar to polarography. See also **Analysis (Chemical)**.

AMPHETAMINE. Also called methylphenethylamine; 1-phenyl-2-aminopropane; Benzedrine; formula $C_6H_5CH_2CH(NH_2)CH_3$; *amphetamine* is a colorless, volatile liquid with a characteristic strong odor and slightly burning taste. Boils and commences decomposition at 200–203°C. Low flash point, 26.7°C. Soluble in alcohol and ether; slightly soluble in water. Amphetamine is the basis of a group of hallucinogenic, habit-forming drugs that affect the central nervous system. The drug also finds medical application, notably in appetite suppressants. It should be emphasized that administration of amphetamines for prolonged periods in connection with weight-reduction programs may lead to drug dependence. Professionals must pay particular attention to the possibility of persons obtaining amphetamines for nontherapeutic use or distribution to others.

AMPHIBOLE. This is the name given to a closely related group of minerals all showing in common a prismatic cleavage of 54–56° as well as similar optical characteristics and chemical composition.

The amphiboles may be said to represent chemically a series of metasilicates corresponding to the general formula $RSiO_3$ where R may be calcium, magnesium, iron, aluminum, titanium, sodium, or potassium. The crystals of the amphibole family group fall within both the monoclinic and orthorhombic systems.

There is a clear parallelism between the amphiboles and the pyroxenes. There are two basic differences between the minerals of these two family groups; amphiboles with cleavage angles of 56° and 124°, with essential OH groups in their structure; pyroxenes with cleavage angles of 87° and 93°, and being anhydrous, with no OH content. Amphibole crystals are usually long and slender and tend to be simple while pyroxene crystals tend to be complex, short, and stout prisms.

Amphibole is common in both lavas and deep-seated rocks, though less so in the basic lavas than pyroxene. Many of the amphiboles may be developed as metamorphic minerals. The following members of the amphibole group are described under their own headings: actinolite, anthophyllite, cummingtonite, glaucophane, grunerite, hornblende, riebeckite and tremolite. Amphibole was so named by Haüy from the Greek word, meaning doubtful, because of the many varieties of this mineral. See also **Pyroxene**.

AMPHIBOLITE. The amphibolites form a large group of rather important rocks of metamorphic character. As the name implies they are made up very largely of minerals of the amphibole group. There may be also a variety of other minerals present, such as quartz, feldspar, biotite, muscovite, garnet, or chlorite in greater or lesser amounts.

Depending upon the particular amphibole present these rocks may be light to dark green or black, the amphibole usually being in long slender prisms or laths, often quite coarse, sometimes in acicular or fibrous forms.

Because the mineral constituents are arranged parallel to the schistosity, amphibolites may have a strongly developed cleavage.

The occurrence of amphibolites accompanying gneisses, schists, and other metamorphic rocks of probable sedimentary origin strongly suggests a similar derivation. Yet some amphibolites cut other metamorphic rocks in the manner of dikes or sills. It is very likely that they have been derived from both original igneous and sedimentary rocks. Large masses of amphibolite suggest gabbroic stocks. Well-known areas in which amphibolites are found are New England, New York State, Canada, Scotland, and the Alps.

AMPHIPATHY. The simultaneous attraction and repulsion in a single molecule or ion consisting of one or more groups having an affinity for the phase in which they are dissolved together with groups that tend to be expelled by the medium.

AMPHIPHILIC. Molecule having a water-soluble polar head (hydrophilic) and a water-insoluble organic tail (hydrophobic), e.g., octyl alcohol, sodium stearate. Such molecules are necessary for emulsion formation and for controlling the structure of liquid crystals.

See also **Emulsions**; and **Liquid Crystals**.

AMPHIPROTIC. Capable of acting either as an acid or as a base, i.e., as a proton donor or acceptor, according to the nature of the environment. Thus, aluminum hydroxide dissolves in acids to form salts of aluminum, and it also dissolves in strong bases to form aluminates. Solvents like water, which can act to give protons or accept them, are amphiprotic solvents. See **Acids and Bases**; and **Salt**.

AMPHOLYTE. A substance that can ionize to form either anions or cations and thus may act as either an acid or a base. An ampholytic detergent is cationic in acid media and anionic in base media. Water is an ampholyte.

AMPOULE. Sometimes spelled ampule, a small sealed glass container for drugs that are to be given by injection. As they are completely sealed, the contents are kept in their original sterile condition.

AMYGDALOID. A vesicular rock, commonly lava, whose cavities have become filled with a secondary deposit of mineral material such as quartz, calcite, and zeolites. The term is derived from the Greek word meaning almond in reference to the frequent almondlike appearance of the filled vesicles, which are called amygdales or amygdules.

AMYL. The 5-carbon aliphatic group C_5H_{11}, also known as pentyl. Eight isometric arrangements (exclusive of optical isomers) are possible. The amyl compounds occur (as in fusel oil) or are formed (as from the petroleum pentanes) as mixtures of several isomers, and, since their boiling points are close and their other properties similar, it is neither easy nor usually necessary to purify them.

See also **Amyl Alcohols**.

AMYL ALCOHOLS. Amyl alcohol describes any saturated aliphatic alcohol containing five carbon atoms. This class consists of three pentanols, four substituted butanols, and a disubstituted propanol, i.e., eight structural isomers $C_5H_{12}O$: four primary, three secondary, and one tertiary alcohol. In addition, 2-pentanol, 2-methyl-1-butanol, and 3-methyl-2-butanol have chiral centers and hence two enantiomeric forms.

The odd-carbon structure and the extent of branching provide amyl alcohols with unique physical and solubility properties and often offer ideal properties for solvent, surfactant, extraction, gasoline additive, and fragrance applications. Amyl alcohols have been produced by various commercial processes in past years. Today the most important industrial process is low pressure rhodium-catalyzed hydroformylation (oxo process) of butenes.

Mixtures of isomeric amyl alcohols (1-pentanol and 2-methyl-1-butanol) are often preferred because they are less expensive to produce commercially; also, the different degree of branching of the mixture imparts a more desirable combination of properties. One such mixture is a

TABLE 1. THE AMYL ALCOHOLS AND SOME OF THEIR PHYSICAL PROPERTIES

Properties	1-Pentanol	2-Pentanol	3-Pentanol	2-Methyl-1-butanol	3-Methyl-1-butanol	2-Methyl-2-butanol	3-Methyl-2-butanol	2,2-Dimethyl-1-propanol
common name	*n*-amyl alcohol	*sec*-amyl alcohol			isoamyl alcohol	*tert*-amyl alcohol		neopentyl alcohol
critical temperature, °C	315.35	287.25	286.45	291.85	306.3	272.0	300.85	276.85
critical pressure, kPa[a]	3868	3710	3880	3880	3880	3880	3960	3880
critical specific volume, mL/mol	326.5	328.9	325.3	327	327	327	327	327
critical compressibility	0.25810	0.26188	0.27128	0.27009	0.26335	0.27992	0.27133	0.27745
boiling point at pressure, °C								
101.3 kPa[a]	137.8	119.3	115.3	128.7	130.5	102.0	111.5	113.1
40 kPa	111.5	93.8	90.9	103.5	105.6	78.3	87.2	89.0
1.33 kPa	44.6	32.0	27.7	40.2	43.0	21.0	26.0	25.0
vapor pressure[b], kPa[a]	0.218	0.547	0.761	0.274	0.200	1.215	0.810	0.929
melting point, °C	−77.6	−73.2	−69.0	< −70	−117.2	−8.8	forms glass	54.0
heat of vaporization at normal boiling point, kJ/mol[c]	44.83	43.41	42.33	44.75	43.84	40.11	41.10	41.35
ideal gas heat of formation[d], kJ/mol[c]	−298.74	−313.80	−316.73	−302.08	−302.08	−329.70	−314.22	−319.07
liquid density[b], kg/m^3	815.1	809.4	820.3	819.1	810.4	809.6	818.4	851.5[e]
liquid viscosity[b], mPa·s(= cP)	4.06	4.29	6.67	5.11	4.37	4.38	3.51[d]	2.5[e]
surface tension[b], mN/m(= dyn/cm)	25.5	24.2	24.6	25.1[d]	24.12	22.7	23.0[d]	14.87[e]
refractive index[d]	1.4080	1.4044	1.4079	1.4086	1.4052	1.4024	1.4075	1.3915
solubility parameter[d], (MJ/m^3)$^{0.5}$[f]	22.576	21.670	21.150	22.274	22.322	20.758	21.607	19.265[e]
solubility in water[b], wt%	1.88	4.84	5.61	3.18	2.69	12.15	6.07	3.74
solubility of water in[b], wt%	9.33	11.68	8.19	8.95	9.45	24.26	11.88	8.23

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] At 20°C unless otherwise noted.

[c] To convert kJ/mol to cal/mol, multiply by 239.

[d] At 25°C.

[e] At the melting point.

[f] To convert (MJ/m^3) to (cal)$^{0.5}$, divide by 2.045.

commercial product sold under the name Primary Amyl Alcohol by Union Carbide Chemicals and Plastics Company Inc.

Physical Properties

With the exception of neopentyl alcohol (mp 53°C), the amyl alcohols are clear, colorless liquids under atmospheric conditions, with characteristic, slightly pungent and penetrating odors. They have relatively higher boiling points than ketonic or hydrocarbon counterparts and are considered intermediate boiling solvents for coating systems (Table 1).

Commercial primary amyl alcohol is a mixture of 1-pentanol and 2-methyl-1-butanol, in a ratio of ca 65 to 35 (available from Union Carbide Chemicals and Plastics Company Inc. in other ratios upon request). Typical physical properties of this amyl alcohol mixture are listed in Table 2.

Like the lower alcohols, amyl alcohols are completely miscible with numerous organic solvents and are excellent solvents for nitrocellulose, resin lacquers, higher esters, and various natural and synthetic gums and resins. However, in contrast to the lower alcohols, they are only slightly soluble in water. Only 2-methyl-2-butanol exhibits significant water solubility.

Chemical Properties

The amyl alcohols undergo the typical reactions of alcohols which are characterized by cleavage at either the oxygen—hydrogen or carbon—oxygen bonds. Important reactions include dehydration, esterification, oxidation, amination, etherification, and condensation.

Manufacture

Three significant commercial processes for the production of amyl alcohols include separation from fusel oils, chlorination of C-5 alkanes with subsequent hydrolysis to produce a mixture of seven of the eight isomers (Pennsalt), and a low pressure oxo process, or hydroformylation, of C-4 olefins followed by hydrogenation of the resultant C-5 aldehydes.

The oxo process is the principal one in practice today; only minor quantities, mainly in Europe, are obtained from separation from fusel oil. *tert*-Amyl alcohol is produced on a commercial scale in lower volume by hydration of amylenes (Dow, BASF).

Health and Safety Factors

The main effects of prolonged exposure to amyl alcohols are irritation to mucous membranes and upper respiratory tract, significant depression of the central nervous system, and narcotic effects from vapor inhalation or oral absorption. All the alcohols are harmful if inhaled or swallowed, appreciably irritating to the eyes and somewhat irritating to uncovered skin on repeated exposure. Prolonged exposure causes nausea, coughing, diarrhea, vertigo, drowsiness, headache, and vomiting. 3-Methyl-1-butanol has demonstrated carcinogenic activity in animal studies.

All of the amyl alcohols are TSCA and EINECS (European Inventory of Existing Commercial Chemical Substances) registered.

The amyl alcohols are readily flammable substances; *tert*-amyl alcohol is the most flammable (closed cup flash point, 19°C). Their vapors can form explosive mixtures with air.

TABLE 2. PHYSICAL PROPERTIES OF PRIMARY AMYL ALCOHOL, MIXED ISOMERS

Property	Value[a]
molecular weight	88.15
boiling point at 101.13 kPa[b], °C	133.2
freezing point, °C	−90[c]
specific gravity 20/20°C	0.8155
absolute viscosity at 20°C, mPa·s(= cP)	4.3
vapor pressure at 20°C, kPa[b]	0.27
flash point (closed cup), °C	45
solubility at 20°C, by wt%	
in water	1.7
water in	9.2

[a] 65/35 blend, i.e., a mixture of 1-pentanol and 2-methyl-1-butanol, 65/35 wt%, respectively.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] Sets to glass below this temperature.

Shipping and Storage

Amyl alcohols are best stored or shipped in either aluminum, lined steel, or stainless steel tanks.

Economic Aspects

All eight amyl alcohol isomers are available from fine chemical supply firms in the United States. Five of them, 1-pentanol, 2-pentanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and 2-methyl-2-butanol (*tert*-amyl alcohols) are available in bulk in the United States; in Europe all but neopentyl alcohol are produced.

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Union Carbide Chemicals and Plastics Company Inc.

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AMYLOSE. See **Starch**.

ANABOLIC AGENTS. See **Steroids**.

ANAEROBE. An organism that can grow in the absence of free oxygen and referred to as an anaerobic organism. Subdivided into *facultative anaerobes*, which can grow and utilize oxygen when it is present; and obligatory anaerobes, which cannot tolerate even a trace of oxygen in their surroundings. Yeast is an example of a facultative anaerobe. Yeast can grow and utilize oxygen in its metabolism, in which case it utilizes all the energy in a carbohydrate and yields water and carbon dioxide. In the absence of oxygen, the yeast cells turn to fermentation and anaerobic metabolism wherein the carbohydrate is converted into alcohol and carbon dioxide. The bacterium which produces botulism in “preserved” foods is an obligatory anaerobe (*Clostridium botulinum*).

In addition to botulism, other species of Clostridium are the etiological agents of tetanus, gas gangrene, and a variety of animal diseases including struck, lamb dysentery, pulpy kidney, and enterotoxemia. The pathogenesis of the clostridia depends largely on the production of potent toxins. Generally, these are heat labile exotoxins and often several pharmacologically and immunologically different toxins may be produced by the same species. In recent years, certain of the toxins have been purified to the point of crystalline purity and revealed to be high-molecular-weight proteins. The availability of the pure toxins has permitted more precise studies both of the chemical nature of the toxin and also of their properties as enzymes. From such toxins, it is possible to produce efficient toxoids for use in prophylactic immunization measures for tetanus and botulism. Some clostridia, in contrast, are beneficial. In addition to the nitrogen-fixing ability of certain species, *C. sporogenes* is active in the decomposition of proteins and contributes to biodegradability of substances, particularly of plant remains. *C. acetobutyleium* is active in production of acetone and butyl alcohol by fermentation.

Glucose can be broken down through glycolysis into pyruvic acid, but in the absence of oxygen as a final acceptor for the hydrogen, the pyruvic acid cannot enter the tricarboxylic acid cycle for further breakdown. Instead the pyruvic acid itself serves as an acceptor for the hydrogen split off in glycolysis. Hence, much less energy is obtained from food in anaerobic metabolism. Lactic acid, alcohol, and some extremely poisonous substances are products of anaerobic metabolism.

In addition to the one-celled anaerobes, certain parasitic worms, such as *Ascaris*, are thought to use anaerobic metabolism, to a certain extent at least. Living in the intestine of higher animals these worms have little access to free oxygen.

The muscles of higher animals are also known to use anaerobic metabolism when the demands on the muscles for energy are greater than can be supplied through the available oxygen. Lactic acid is generated.

The diverse mechanisms that permit animal life in the absence of oxygen are described in considerable detail by P.W. Hochachka (“Living without Oxygen,” Harvard Univ. Press, Cambridge, Massachusetts, 1980).

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ANALCIME. A common zeolite mineral, $NaAlSi_2O_6 \cdot H_2O$, a hydrous soda-aluminum silicate. It crystallizes in the isometric system, hardness, 5–5.5; specific gravity, 2.2; vitreous luster; colorless to white; but may be grayish, greenish, yellowish, or reddish. Its trapezohedral crystal resembles garnet but is softer; it is distinguished from leucite only by chemical tests.

There are many excellent European localities. Magnificent crystals occur at Mt. St. Hilaire, Quebec, Canada; in the United States at Bergen Hill and West Paterson, New Jersey, Keweenaw County, Michigan, and Jefferson County, Colorado. Nova Scotia furnishes beautiful specimens.

Analcime is a relatively common mineral and occurs with other zeolites in cavities and fissures in basic igneous rocks, occasionally in granites or gneisses. It seems to occur as a replacement and perhaps in some cases as a primary mineral crystallizing from a magma rich in soda and water vapor under pressure. The name analcime is derived from the Greek word meaning weak, in reference to the weak electric charge developed when heated or subjected to friction.

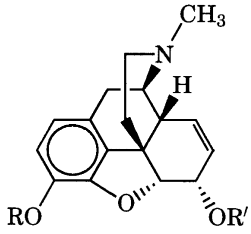
ANALGESICS, ANTIPYRETICS, AND ANTIINFLAMMATORY AGENTS. Pain, pyresis, and inflammation are distinct physiological responses which can occur independently; they are often associated as the body mounts a response to an injury or insult. Each is an important signal from injured tissue and the signal's continued presence can guide a physician in diagnosing and treating the condition which led to the occurrence.

The twentieth century has seen considerable progress in the understanding of pain and inflammation and the relationship of one to the other. It is increasingly apparent that the central and peripheral nervous systems are capable of causing the production of mediators which can attract and activate inflammatory cells, thereby initiating or amplifying an inflammatory response. At the same time, inflammatory cells are also capable of releasing substances which not only respond to the original insult, but also stimulate the nervous systems.

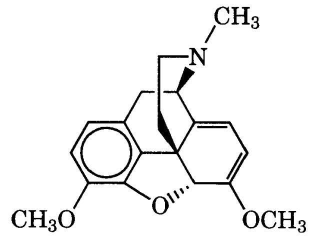
A number of interdependent physiological mechanisms, each providing new targets for therapeutic intervention, and allowing for the development of new treatments for pain, pyresis, and inflammation, have been discovered. At least eight distinct types of opioid receptors have been identified and the corresponding individual functions are beginning to be understood. Moreover, a great deal has been learned about the role of lipid mediators in the inflammatory response and how antiinflammatory agents control their production.

Opioid Agonists

Opium is the dried, powdered sap of the unripe seed pod of *Papaver somniferum*, a poppy plant indigenous to Asia Minor. More than 20 different alkaloids (qv) of two different classes comprise 25% of the weight of dry opium. The benzylisoquinolines, characterized by papaverine (1.0%), a smooth muscle relaxant, and noscapine (6.0%), an antitussive agent, do not have any analgesic effects. The phenanthrenes, the second group, are the more common and include 10% morphine (**1**, $R' = R = H$), 0.5% codeine, $C_{18}H_{21}NO_3$, (**1**, $R' = H$, $R = CH_3$), and 0.2% thebaine, $C_{19}H_{21}NO_3$, (**2**).



(**1**)



(**2**)

Morphine, mol wt 285.3, effectively relieves pain and increases an individual's ability to tolerate a painful experience. It also produces a remarkably broad range of other effects, including drowsiness, mood changes, respiratory depression, nausea, decreased gastrointestinal motility, and vomiting. Morphine behaves as a receptor agonist, acting preferentially at the μ receptor, but also exhibiting appreciable affinity for other opioid receptors. A standard therapeutic dose is 10–15 mg, usually administered subcutaneously. Analgesia peaks in about one hour and lasts for four to five hours. An important feature of morphine and related drugs is the development of physical dependence on, and tolerance to, some of the effects.

Codein, mol wt 299.3, is a significantly less potent analgesic than morphine, requiring 60 mg (0.20 mmol) to equal the effectiveness of 10 mg (0.04 mmol) of morphine. However, codeine is orally effective, and it is less addictive and associated with less nausea than morphine.

Introduced in 1898, heroin (**1**, $R = R' = COCH_3$) was heralded as a nonaddictive alternative to morphine. Subsequent clinical experience showed it to be highly addictive and preferred by addicts over morphine.

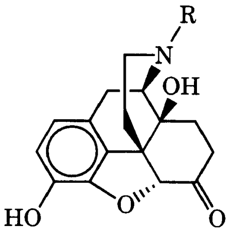
Synthetic and Semisynthetic Agonists

In attempts to discover drugs demonstrating fewer undesirable side effects than morphine, many synthetic analogues have been prepared. Some of these are shown in Table 1.

Several common structural features necessary for opioid, analgesic activity have been identified from the action of the analogues. Systematic simplification demonstrated that much of the morphine ring structure could be modified or even eliminated. The piperidine ring, in a chair conformation, and in particular the nitrogen atom of that ring, appears essential to pharmacological activity. The nitrogen is believed to attach to an anionic center in the receptor. Also crucial is the presence of the phenyl ring which, through van der Waals forces, binds to the hydrophobic portion of the receptor.

Opioid Antagonists and Partial Agonists

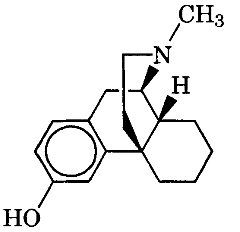
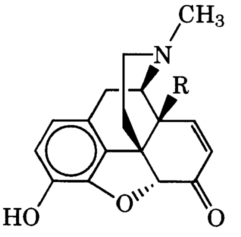
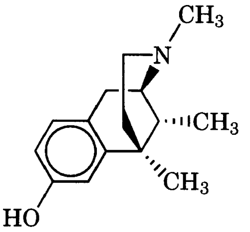
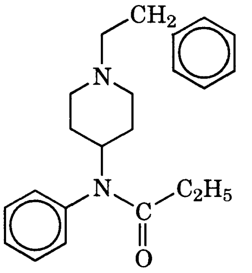
The replacement of the *N*-methyl group on the nitrogen atom of the piperidine ring of morphine and analogues, by allyl, isopropyl, or methyl cyclopropyl, an isopropyl isostere, results in compounds which antagonize opioid responses, especially respiratory depression. Naloxone (**7**), $C_{19}H_{21}NO_4$, and naltrexone (**8**), $C_{20}H_{23}NO_4$, are both derived from oxymorphone (Table 1) and exhibit agonist activity only at doses that are of little clinical significance. In the absence of opioid drugs, naloxone does not cause analgesia, respiratory depression, or sedation. However, when administered with an opioid analgesic, the effects produced by the opioid agonist are promptly reversed. The ability to antagonize opioids at all of the different opioid receptors makes naloxone useful for the treatment of opioid overdose. Naltrexone has a similar profile, but it is orally active and has a significantly longer half-life.

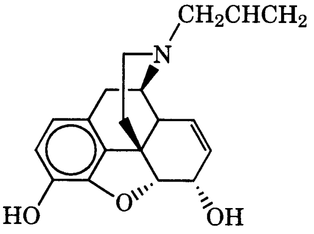


(**7**)

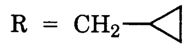
$R = CH_2CHCH_2$

TABLE 1. SYNTHETIC MORPHINE ANALOGUES

Name	Molecular formula	Structure
levorphanol	$C_{17}H_{23}NO$	 **(3)**
hydromorphone	$C_{17}H_{19}NO_3$	 **(4, R = H) (4, R = OH)**
oxymorphone	$C_{17}H_{19}NO_4$	
phenazocine	$C_{22}H_{27}NO$	 **(5)**
fentanyl	$C_{22}H_{29}NO_2$	 **(6)**



(**8**)



$R = CH_2-\triangleleft$

The quest for compounds that combined the analgesic properties of morphine, were nonaddictive and lacked side effects, led to the development of the drugs that have both agonist and antagonist activities. Nalbuphine and buprenorphine are semisynthetic materials derived from oxymorphone and thebaine respectively, whereas pentazocine and butorphanol are benzomorphan and morphan derivatives. Although structurally similar, they display different receptor affinities: pentazocine is a weak μ-antagonist, but a strong agonist of the κ-receptor; nalbuphine is a competitive antagonist for the μ-receptor, blocking the effects of the morphinelike drugs, but is a partial agonist for the κ and ς receptors; and buprenorphine is a partial agonist for the μ-receptor.

Pharmacologically, the effects of these drugs resemble those of opioid agonists. All four have analgesic potency equal to or greater than morphine and, like morphine, they cause respiratory depression. A ceiling effect is reached, however, above which increased doses do not increase respiratory depression or do not produce proportionally greater depression.

Other Analgesic Agents

Most analgesic agents rely on agonism of the μ receptor for their activity, however the ability of the κ and δ receptors to induce analgesia is also well documented. Some nonmorphine analgesics which may preferentially bind to κ and δ receptors are found in Table 2.

Antiinflammatories and Antipyretics

Most of the time, the powerful analgesia supplied by morphine and the other opioid analgesics is not needed. Rather, a mild analgesic, such as aspirin, the most commonly employed analgesic agent, can be used for the treatment of simple pain associated with headaches, minor muscle pain, mild trauma, arthritis, cold and flu symptoms, and fever.

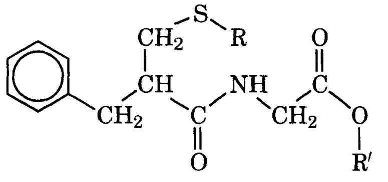
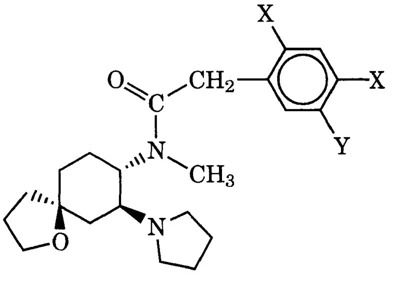
Aspirin, the oldest of the nonsteroidal antiinflammatory drugs (NSAIDs), is a member of the salicylate group.

Aspirin's pain relief results, not through direct action on the central nervous system, but rather through peripheral action. It has been proposed that aspirin and aspirinlike drugs inhibit the enzymatic production of prostaglandins, a group of endogenous agents which are well known to cause erythema, edema, pain, and fever. Aspirin does not act as a prostaglandin receptor antagonist; rather it blocks the cyclooxygenase enzymecatalyzed conversion of arachidonic acid, $C_{20}H_{32}O_2$, to cyclic endoperoxides, a prostaglandin precursor.

The action of endogenous pyrogens on the hypothalamus produces fever, because of a readjustment in the central set point controlling the body's internal temperature. Salicylates and other NSAIDs achieve their antipyretic effect by controlling the prostaglandin-induced release of pyrogens.

A second class of NSAIDs, the so-called coal-tar analgesics, are derived from acetanilide. Although it is no longer used therapeutically, its analogues, phenacetin and the active metabolite, acetaminophen, are effective alternatives to aspirin. They have analgesic and antipyretic effects that do not differ significantly from aspirin, but they do not cause the gastric irritation, erosion, and bleeding that may occur after salicylate treatment.

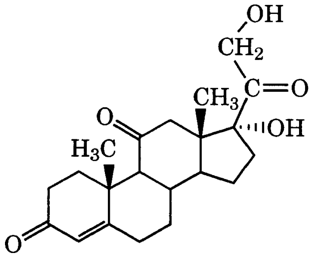
TABLE 2. NONMORPHINE ANALGESICS

Name	Molecular formula	Structure
acetorphan	$C_{21}H_{23}NO_4S$	 **(9, R = COCH$_3$, R′ = CH$_2$C$_6$H$_5$) (9, R = H, R′ = H)**
thiorphan	$C_{12}H_{15}NO_3S$	
spiradoline	$C_{22}H_{30}Cl_2N_2O_2$	 **(10, X = H, Y = Cl)**

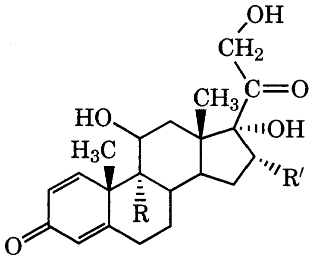
In contrast to aspirin, however, they are not cyclooxygenase inhibitors and have no antiinflammatory properties. Clinically, acetaminophen is preferred over phenacetin, because it has less overall toxicity.

A more recently introduced, nonprescription analgesic is the aryl propionic acid, ibuprofen, which offers significant advantages over aspirin. Ibuprofen, a cyclooxygenase inhibitor, displays good antiinflammatory activity. It is more potent than aspirin and has a lower incidence of gastrointestinal irritation, although at high doses or chronic exposure, gastric irritation, as well as some renal toxicity, has been observed. Ibuprofen is more effective than propoxyphene in relieving episiotomy pain, pain following dental extractions, and menstrual pain.

The adrenal cortex produces steroidal hormones that are associated with carbohydrate, fat, and protein metabolism, electrolyte balance, and gonadal functions. One of these, cortisone, $C_{21}H_{28}O_5$ (**11**), demonstrated a remarkable ability to relieve the symptoms of inflammatory conditions. Other glucocorticoid steroids, such as dexamethasone, $C_{22}H_{29}FO_5$ (**12**, R = F, R′ = CH_3), and prednisolone, $C_{21}H_{28}O_5$ (**12**, R = R′ = H), also have antiinflammatory properties.



(**11**)



(**12**)

These steroids are capable of preventing or suppressing the development of the swelling, redness, local heat, and tenderness which characterize inflammation.

Unfortunately steroids merely suppress the inflammation while the underlying cause of the disease remains. Another serious concern about steroids is that of toxicity. The abrupt withdrawal of glucocorticoid steroids results in acute adrenal insufficiency. Long-term use may induce osteoporosis, peptidic ulcers, the retention of fluid, or an increased susceptibility to infections. Because of these problems, steroids are rarely the first line of treatment for any inflammatory condition, and their use in rheumatoid arthritis begins after more conservative therapies have failed.

Economic Aspects

Analgesics and antiarthritics represent significant worldwide pharmaceutical markets. Table 3 lists trade names and producers of some of the more commercially important agents.

See also **Alkaloids**; **Aspirin** and **Morphine**.

Richard A. Nugent
Charles M. Hall
Upjohn Company

TABLE 3. TRADE NAMES AND PRODUCERS OF ANALGESICS, ANTIPYRETICS, AND ANTIINFLAMMATORY DRUGS

Compound name	Trade name	Producer
levorphanol	Dromoran	Hoffmann-LaRoche
phenazocine	Prinadol	Smith Kline & Beecham
meperidine	Demerol	Winthrop
propoxyphene	Darvon	Eli Lilly
naloxone	Narcan	Du Pont
naltrexone	Trexan	Du Pont
nalbuphine	Nubain	Du Pont
buprenorphine	Buprenex	Norwich Eaton
pentazocine	Talwin	Winthrop
butorphanol	Stadol	Bristol
acetaminophen	Tylenol	McNeil
ibuprofen	Motrin	Upjohn
naproxen	Naprosyn	Syntex
ketoprofen	Orudis	Wyeth
flurbiprofen	Ansaid	Upjohn
indomethacin	Indocin	Merck Sharpe & Dohme
sulindac	Clinoril	Merck Sharpe & Dohme
diclofenac	Voltaren	CIBA-GEIGY
meclofenamate	Meclomen	Parke-Davis
piroxicam	Feldene	Pfizer
diflunisal	Dolobid	Merck Sharpe & Dohme

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ANALYSIS (Chemical). Analytical chemistry is that branch of chemistry concerned with the detection and identification of the atoms, ions, or radicals (groups of atoms which react as a unit) of which a substance is composed, the compounds which they form, and the proportions of these compounds present in a given substance. The work of the analyst begins with sampling, since analyses are performed upon small quantities of material. The validity of the result depends upon the procurement of a sample that is representative of the bulk of material in question (which may be as large as a carload or tankload).

The Revolution in Analytical Chemistry—A Perspective

During the last few decades, not many branches of any science have undergone so much change in the equipment and procedures used as has the field of *chemical analysis*. This revolution also has impacted on how the principles of chemistry are taught today. The revolution in analysis also has had wide influence on technology in general because of the far greater accuracy with which chemical determinations can be made. Just a few years ago, analyses that would yield reliable data in the range of a few parts per million (*ppm*) were considered excellent. The accurate reporting of parts per billion (*ppb*) was achieved in the 1960s. With modern analytical instrumentation available beginning in the 1990s, a part per trillion ($\frac{1}{10^{12}}$) sensitivity was achieved for some routine analyses, as, for example, in determinations of the dangerous pollutant, *dioxin*. A special tandem-accelerator mass spectrometer now can detect three atoms of ^{14}C in the presence of 10^{16} atoms of ^{12}C in a radiocarbon age dating procedure. (It is interesting to note that a pinhead would occupy a part per trillion of the area of a road from New York to California; 10^{12} molecules of molecular weight 600 weigh only 10^{-9} gram.)

While the impact of vastly improved chemical analysis has been felt by essentially all phases of science, dramatically more precise data have been of notable significance in the area of pollutants and pharmaceuticals. The effects of minute impurities, beyond detection just a few years ago, now can be determined and become the basis for pollution and drug legislation, litigation, etc. In some cases, unfortunately, the long-term effects of impurities in substances and in the environment remains a pseudoscience of statistics. Consequently instrumentally yielded analytical chemical information requires caution and prudence in its application to decision making at a policy level.

Traditional Analytical Chemistry

In the interest of putting modern analytical chemistry in perspective, it is in order to review that long time period (essentially prior to the 1940s) when the subject was divided into two readily understood areas: 1. *Qualitative chemical analysis*, in which one is concerned simply with the identification of the constituents of a compound or components of a mixture, sometimes accompanied by observations (rough estimates) of whether certain ingredients may be present in major or trace proportions.

2. *Quantitative chemical analysis*, which is concerned with the amounts (to varying degrees of precision) of all, or frequently of only some, specific ingredients of a mixture or compound. Classically, quantitative chemical analysis is divided into (a) *gravimetric analysis* wherein weight of sample, precipitates, etc., is the underlying basis of calculation, and (b) *volumetric analysis* (titrimetric analysis) wherein solutions of known concentration are reacted in some fashion with the sample to determine the concentration of the unknown. Obviously, the Figure from either gravimetric or volumetric determinations are convertible and the two methodologies frequently are combined in a multistep analytical procedure.

Classical laboratory, manual methods conducted on a macro-scale where sample quantities are in the range of grams and several milliliters. These are the techniques that developed from the earliest investigations of chemistry and which remain effective for teaching the fundamentals of analysis. However, these methods continue to be widely used in industry and research, particularly where there is a large variety of analytical work to be performed. The equipment, essentially comprised of analytical balances and laboratory glassware, tends to be of a universal nature and particularly where budgets for apparatus are limited, the relative modest cost of such equipment is attractive.

A Gradual Break from Tradition

One of the first breaks from traditional analytical chemistry was the addition of *microchemical methods*. These methods essentially extended macro-scale techniques so that they could be applied for determinations involving very small (milligram) quantities of samples. These methods required fully new approaches or extensive modifications of macro-scale equipment. Consequently, the apparatus usually was sophisticated, relatively costly, and required, greater manipulative skills. Nevertheless, microchemical methods opened up entirely new areas of research, making possible the determination of composition where the availability of samples, as in many areas of biochemistry, was confined to very small quantities.

A second major break was the introduction of *semi-automated analytical apparatus* that introduced an interim step between (a) macro-scale and microchemical analysis techniques on the one hand and (b) fully instrumented and automated analytical methods on the other hand. Significant design changes in chemical balances that greatly increased the speed of weighing samples and reagents and automatic and self-refilling burettes are examples of ways in which an analytical procedure could be "tooled" to conserve technician power, reduce drudgery, and often contribute to more reliable and precise results.

Another major break was the introduction of *process analyzers*, which moved the chemical control laboratory from a central location in a materials-manufacturing plant to the use of chemical analyzers *on-line*. With this concept, quality control no longer depended upon grab samples, analyzed periodically and thus always behind (time lag) conditions actually occurring in the process itself at any given instant. Many analytical instruments today, at least in principle, are applicable to on-line installation. While thousands of on-line analyzers are in place, usage throughout the processing and manufacturing industries is far from universal. Difficulties in designing and protecting sensitive instrumentation from the very rugged environments encountered on-line continue. Thus, chemical composition is commonly inferred from other related measurements, such as temperature, pressure, and careful chemical analysis of raw materials at the input side and similar analyses of products on the output side. Numerous techniques used for on-line instrumentation are described in this encyclopedia.

Energy—Matter Interactions in Analytical Instrumentation

Modern chemical analyzers, ranging from research and laboratory applications to process control, developed in a rather chaotic manner over several decades. There indeed was no master plan and, in fact, it was not until the late 1950s that a concerted attempt was made to classify analytical instruments in a scientific way. Table 1 is an updated, but abridged version of a summary prepared and first published in 1957[1]. The thrust of the summary is directed toward industrial instrumentation, although it embraces the principal laboratory instruments as well.

Chemical-composition variables are measured by observing the interactions between matter and energy. That such measurements are possible stems from the fundamental that all known matter is comprised of complex, but systematic arrangements of particles which have mass and electric charge. Thus, there are neutrons that have mass but no charge; protons that have essentially the same mass as neutrons with a unit positive charge; and electrons that have a negligible mass with a unit negative charge. The neutrons and protons comprise the nuclei of atoms. Each nucleus ordinarily is provided with sufficient orbital electrons, in what is often visualized as a progressive shell-like arrangement of different energy levels, to neutralize the net positive charge on the nucleus. The total number of protons plus neutrons determines the atomic weight. The number of protons, which, in turn, fixes the number of electrons, determines the chemical properties and the physical properties, except mass, of the resulting atom.

The chemical combinations of atoms into molecules involve only the electrons and their energy states. Chemical reactions involving both structure and composition generally occur by loss, gain, or sharing of electrons among the atoms. Thus, every configuration of atoms in a molecule, crystal, solid, liquid, or gas may be represented by a specific system of electron energy states. Also, the particular physical state of the molecules, as resulting from their mutual arrangement, also is reflected upon these energy states. Fortunately, these energy states, characteristic of the composition of any particular substance, can be inferred by observing the consequences of interaction between the substance and an external source of energy.

External energy sources used in analytical instrumentation include:

1. electromagnetic radiation; 2. electric or magnetic fields; 3. chemical affinity or reactivity; 4. thermal energy; and 5. mechanical energy.

The interaction of electromagnetic radiation with matter yields fundamental information as the result of the fact that photons of electromagnetic radiation are emitted or absorbed whenever changes take place in the quantized energy states occupied by the electrons associated with atoms and molecules. X-rays (photons or electromagnetic wave packets with relatively high energy) penetrate deeply into electron orbits of an atom and provide, upon absorption, the large quantity of energy required to excite one of the innermost electrons. Thus, the pattern of x-ray excitation or absorption is relative to the identity of those atoms whose orbital electrons are excited, ideally suiting x-ray techniques for determining atoms and elements in dense samples. But, because of the penetrating power of x-rays, they are not suited to the excitation of low-energy states that correspond to outer-shell or valence electrons; or of the inter-atomic bonds which involve vibration or rotation.

In contrast, the relatively longer wavelengths of infrared radiation (photons having relatively low energy) correspond to the energy transformations involved in the vibration of atoms in a molecule as resulting from stretching or twisting of the inter-atomic bonds. Thus, because the penetrating power of electromagnetic radiation varies over the total spectrum, an instrumental irradiation technique can be developed for almost any analytical instrumentation requirement.

The interaction of matter with electric or magnetic fields is widely applied for determining chemical composition. The mass spectrometer, for example, which uses a combination of electric and magnetic fields to sort out constituent ions in a sample, takes full advantage of this interaction. A simple electric-conductivity apparatus determines ions in solution as the result of applying an electric potential difference across an electrolyte.

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[1] Albright, C.M., Jr., "Chemical Composition," in *Process Instruments and Controls Handbook*, D.M. Considine, Editor, McGraw-Hill, New York, 1957. The book is now in its 5th edition (1999).

TABLE 1. INTERACTIONS BETWEEN ENERGY AND MATTER UTILIZED IN ANALYTICAL INSTRUMENTATION

GROUP I—INTERACTIONS WITH ELECTROMAGNETIC RADIATION

Measurement of the quantity and quality of electromagnetic radiation emitted, reflected, transmitted, or diffracted by the sample.

Electromagnetic radiation varies in energy with radiation frequency, that of the highest frequency or shortest wavelength having the highest energy and penetration into matter. Radiation of the shortest wavelengths (gamma rays) interacts with atomic nuclei; x-rays with the inner shell electrons; visible and ultraviolet light with valence electrons and strong interatomic bonds; and infrared radiation and microwaves with the weaker interatomic bonds and with molecular vibrations and rotation. Most of these interactions are structurally related and unique. They may be used to detect and measure the elemental or molecular composition of gas, liquid, and solid substances within the limitations of available equipment.

Emitted Radiation
Thermally Excited: Optical emission spectro-chemical analysis
  Flame photometry
Electro-magnetically Excited: Fluorescence
  Raman spectro-photometry
  Induced radioactivity
  X-ray fluorescence
Transmitted and Reflected Radiation
  X-ray analysis
  Ultraviolet spectro-photometry
  Ultraviolet absorption analysis
  Conventional photometry—transmission colorimetry
  Colorimetry
  Light scattering techniques
  Optical rotation-polarimetry
  Refractive index
  Infrared spectro-photometry
  Infrared process analyzers
  Microwave spectroscopy
  Gamma ray spectroscopy
  Nuclear quadrupole moment

GROUP II—INTERACTION WITH CHEMICALS

Measurement of the results of reaction with other chemicals in terms of amount of sample or reactant consumed, product formed, or thermal energy liberated, or determination of equilibrium attained.

The selectivity inherent in the chemical affinity of one element or compound for another, together with their known stoichiometric and thermodynamic behavior, permits positive identification and analysis under many circumstances. In a somewhat opposite sense, the apparent dissociation of substances at equilibrium in chemical solution gives rise to electrically measurable valence potentials, called oxidation-reduction potentials, whose magnitude is indicative of the concentration and composition of the substance. While individually all the above effects are unique for each element or compound, many are readily masked by the presence of more reactive substances so they can be applied only to systems of known composition limits.

Consumption of Sample or Reactant
  Orsat analyzers
  Automatic titrators
Measurement of Reaction Products
  Impregnated paper-tape devices
  Photometric reaction product analyzers
Thermal Energy Liberation
  Combustion-type analyzers
  Total combustibles analyzers (hydrocarbons and carbon monoxide analyzers)
Equilibrium Solution Potentials
  Redox potentiometry
  pH (hydrogen ion concentration)
  Metal ion equilibria

GROUP III—REACTION TO ELECTRIC AND MAGNETIC FIELDS

Measurement of the current, voltage, or flux changes produced in energized electric and magnetic circuits containing the sample.

The production of net electric charge on atoms or molecules by bombardment with ionizing particles or radiation or by electrolysis or dissociation in solution or the induction of dipoles by strong fields establishes measurable relationships between these ionized or polarized substances and electric and magnetic energy. Ionized gases and vapors can be accelerated by applying electric fields, focused or deflected in magnetic fields, and collected and measured as anelectric current in mass spectroscopy. Ions in solution can be transported, and deposited if desired, under the influence of various applied potentials for coulometric or polarographic analysis and for electrical conductivity measurements. Inherent and induced magnetic properties give rise to specialized techniques, such as oxygen analysis based on its paramagnetic properties and nuclear magnetic resonance, which is exceedingly precise and selective for determination of the compounds of many elements.

Mass Spectroscopy
  Quadrupole mass spectrometry
Electrochemical
  Reaction product analyzers
Electrical Properties
  Electrical conductivity/electrical resistivity
  Dielectric constant and loss factor
  Oscillometry
  Gaseous conduction
Magnetic Properties
  Paramagnetism
  Nuclear magnetic resonance
  Electron paramagnetic resonance

GROUP IV—INTERACTION WITH THERMAL OR MECHANICAL ENERGY

Measurement of the results of applying thermal or mechanical energy to a sample in terms of energy transmission, work-done, or changes in physical state.

The thermodynamic relationship involving the physical state and thermal energy content of any substance permits analysis and identification of mixtures of solids, liquids, and gases to be based on the determination of freezing or boiling points and on the quantitative measurement of physically separated fractions. Useful information can often be derived from thermal conductivity and viscosity measurements, involving the transmission of thermal and mechanical energy, respectively.

Effects of Thermal Energy
  Thermal conductivity
  Melting and boiling point determinations
  Ice point-humidity instrumentation, among others
  Dew point-humidity instrumentation, among others
  Vapor pressure
  Fractionation
  Chromatography
  Thermal expansion
Effects of Mechanical Energy or Forces
  Viscosity
  Sound velocity
  Density and specific gravity

The use of chemical reactions in analytical instrumentation essentially extends the fundamental techniques of older laboratory analytical methods.

Numerous analytical instrumentation techniques involve interactions between mechanical and thermal energy with matter. All of these interactions are summarized in the accompanying table.

Targets of Analytical Instrumentation

Some authorities feel that less emphasis and even abandonment by some educational institutions of the traditional qualitative-analysis (wet basis) course represents the loss of a great learning experience in the fundamentals of chemistry. Generally, for teaching purposes, the course is limited to inorganic substances. Practically all of the fundamentals of inorganic chemistry are called upon in the execution of qualitative analysis. Thus, in addition to serving as an effective analytical procedure, the method is an effective teacher.

The first important step is that of putting the sample (unknown) into solution. For metals and alloys, strong acids, such as HCI, HNO_3, or aqua regia may be used. If the material is not fully dissolved by these acids, it should be fused, either with sodium carbonate (alkaline fusion) or potassium acid sulfate (acid fusion). Care should be exercised to make certain that no portion of the unknown is volatilized and thus lost during these procedures.

The next step is the detection of the cations of the metals. For this purpose, the solution should be treated with HNO_3, by evaporation and re-dissolving if necessary, to remove other acid radicals, so that nitrate is the only anion present in the solution. Then, a systematic procedure is followed for separation of groups of the cations. Such schemes of separation have been devised for all the metals found in nature. A shortened plan, which applies to 24 of the commonly occurring metals and ammonium, has been known and practiced for many years. This plan consists of the separation of the 24 metals into five groups. Further details of the procedure are given in the 6th Edition of this encyclopedia.

Criteria for Selecting Appropriate Analytical Method

These include (1) sensitivity, (2) specificity, (3) speed, (4) sampling methodology re quired, (5) simplicity (translated into terms of expertise needed), and, of course, cost as traded off against the other criteria.

Sensitivity, as previously mentioned, has improved almost astoundingly over the past few years. Of course, great sensitivity is not always needed, with the ppm and ppb levels well serving many industrial and laboratory requirements. Most frequently, sensitivity is closely related to cost. Sensitivity is also closely related to accuracy, i.e., sensitivity of a reliable, repeatable nature. Sensitivity depends on how well the target of measurement can be transduced into some reliable signal from which the instrument can create a display and/or record. The absorption or emission of photons is the basis of many spectroscopic analytical methods, such as x-ray, ultraviolet, infrared, nuclear magnetic resonance, Raman, Mossbauer, etc., as well as of charged particles, which serve as the basis for electron and mass spectrometry and of the electrochemical, flame ionization, etc. used in chromatography. Through the use of intense energy sources, such as lasers, synchrotron radiation, and plasmas, the efficiency of converting (transducing) the objective parameter of analysis (*analyte*) is greatly improved. McLafferty reports that efficiencies approaching 100% have been experienced for resolution-enhanced multi-photon ionization of atomic and molecular species. Multiplier detectors can respond to the arrival of a single photon or ion. Such methods can detect, for example, a single cesium atom or naphthalene molecule.

Specificity is an ever-present criterion because there are indeed few analytical techniques that detect single species without careful tuning. Frequently, filtering techniques must be used as a means of narrowing the range of detection. See **Infrared Radiation**; and **Ultraviolet Spectrometers**.

Speed. The rapidity with which an analysis can be performed and utilized (including interpretation, whether manual or automatic) is particularly important in industrial chemical analysis. In a laboratory setting, this may not be quite so urgent, but even then time is a major criterion where, in most cases, special personnel are held up in other activities, awaiting the results of an analysis. Frequently higher cost can be justified on the basis of less time and lower personnel costs per analysis made.

One of the principal contributions of electronic data processing over the past several years in terms of chemical analysis is the saving of manual effort in interpreting analytical data. Special techniques, such as Fourier transform, have increased speed (as well as sensitivity) by orders of magnitude in connection with infrared, nuclear magnetic resonance, and mass spectroscopy. Of course, for on-line process analyses, essentially instantaneous interpretation is required to provide the proper error signal that is used to position the final control element (valve, feeder, damper, etc.).

Sampling for analysis is sometimes considered a secondary criterion in the selection of an analysis system. In the laboratory or on the process, sampling often is the practical key to success. The entire result can depend upon obtaining a *truly representative* sample and the sampling methodology used varies widely with the materials to be analyzed. Sampling of solids, such as coal, metals, etc. differs markedly from sampling for fluids. Particularly in process analyses, where the environment varies and contrasts markedly with the usual laboratory conditions, a gas or liquid will require filtering and temperature and pressure conditioning—so that the composition detector will consistently be exposed to the material in question under the same physical conditions.

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ANALYSIS (Organic Chemical). Various techniques are used in the chemical analysis of organic substances both in microanalysis and macro laboratory procedures. As contrasted with the determination of total carbon content or the amounts of other specific chemical elements, the representative analytical techniques described here are directed toward the determination of presence and amount of various functional groups (radicals). These groups also are described elsewhere in this volume and, in several instances, additional analytical procedures are related.

(1) The *carboxyl group* is determined by titration with standard sodium hydroxide solution, using phenolphthalein as the indicator, by the reaction

$$\mathrm{RCOOH + NaOH \longrightarrow RCOONa + H_2O}$$

(2) The *hydroxyl group* is determined by reaction with acetic anhydride on heating in a sealed tube by the reaction

$$\mathrm{ROH + (CH_3CO)_2O \longrightarrow ROOCCH_3 + CH_3COOH}$$

The amount of hydroxyl group present is found by titrating the resulting acetic acid ($\mathrm{CH_3COOH}$) with standard sodium hydroxide, as in (1).

(3) The *acyl group* ($-\mathrm{COOR}$) in esters and amides is determined by hydrolysis in alcoholic sodium hydroxide solution, followed by ion exchange with an acidic resin. The carboxylic acid formed is then titrated with standard sodium hydroxide, as in (1). The reactions are

$$\mathrm{R\underset{Ester}{COOR'} + NaOH \longrightarrow RCOONa + R'OH}$$

or

$$\mathrm{RCO\underset{Amide}{NHR'} + NaOH \longrightarrow RCOONa + R'NH_2 + H_2O}$$

$$\mathrm{RCOONa + Resin\text{-}SO_3H \longrightarrow RCOOH + Resin\text{-}SO_3Na}$$

(4) The *carbonyl group* is determined by a reaction with 2,4-dinitrophenyl hydrazine which precipitates the 2,4-dinitrophenyl hydrazone of the aldehyde or ketone, which is then filtered off, dried, and weighed. The reaction is

$$\mathrm{RR'CO + H_2NNHC_6H_3(NO_2)_2 \longrightarrow RR'C{:}NNHC_6H_3(NO_2)_2 + H_2O}$$

(5) The *peroxy group* is determined by treatment with sodium iodide. The liberated iodine is then titrated with standard sodium thiosulfate solution. The reaction is

$$\mathrm{RCOO_2OCR + 2\ NaI \longrightarrow I_2 + 2\ R'COONa}$$

(6) The *primary amino group* is determined by treatment with nitrous acid and measurement of the nitrogen (gas) produced by the reaction

$$\mathrm{RNH_2 + HNO_2 \longrightarrow N_2 + ROH + H_2O}$$

(7) The aromatic *nitro group* is determined by its reduction with excess titanium(III) chloride. After the reaction, the unused titanium(III) ions ($\mathrm{Ti^{3+}}$) are determined by titration with iron(III) sulfate or iron alum solution:

$$\mathrm{RNO_2 + 6\ TiCl_3 + 6\ HCl \longrightarrow RNH_2 + 6\ TiCl_4 + 2\ H_2O}$$

$$\mathrm{Ti^{3+} + Fe^{3+} \longrightarrow Ti^{4+} + Fe^{2+}}$$

(8) The *hydrazino group* is determined by oxidation with copper(II) sulfate solution, and measurement of the nitrogen (gas) formed. The reaction is

$$\mathrm{RNHNH_2 + 4\ CuSO_4 + H_2O \longrightarrow N_2 + ROH + 2\ Cu_2SO_4 + H_2SO_4}$$

(9) The *sulfhydryl group* is determined by reaction with iodine, which is produced in the vessel from potassium iodide, added in excess to the solution, and potassium iodate, added from a buret until the completion of the reaction is shown by the permanent appearance of the blue color of starch–iodine.

$$\mathrm{2\ RSH + I_2 \longrightarrow RSSR + 2\ HI}$$

(10) *Unsaturated groups* are determined by addition of bromine, by the reaction

$$\mathrm{R_2C{=}CR'_2 + Br_2 \longrightarrow R_2CBr{-}CBrR'_2}$$

The term *functional group analysis* sometimes is used to describe the foregoing kinds of analyses.

Ultimate Analysis. This term, generally limited to organic chemical analysis, denotes the determination of the proportion of each element in a given substance. The primary determination is that of carbon and hydrogen, which is conducted by mixing the sample with copper(II) oxide and heating it in a stream of oxygen to a temperature of 700 to 800°C. The carbon is converted to carbon dioxide and the hydrogen to water. These products are then absorbed by suitable reagents. For example, magnesium perchlorate dehydrate may be used to absorb water and sodium hydroxide to absorb carbon dioxide. Although the fundamental procedure is simple, a rather elaborate train of apparatus, involving both temperature and flow control, is required. The traditional procedure for determining nitrogen is the Kjeldahl method. The Unterzaucher method is used for determining oxygen in organic substances, the sample is heated to a high temperature (approximately 1120°C) in an atmosphere of nitrogen. Under these conditions, the oxygen present combines with part of the carbon content to form carbon dioxide and with part of the hydrogen content to form water. The gases then are passed over hot carbon (1150°C), whereupon both the carbon dioxide and water are converted to carbon monoxide. The latter gas upon leaving the furnace is passed over iodine pentoxide $\mathrm{I_2O_5}$ at about 110°C to form iodine by the reaction: $\mathrm{5CO + I_2O_5 \longrightarrow I_2 + 5CO_2}$. The freed iodine is titrated with a standard sodium thiosulfate solution.

ANALYZER (Reaction-Product). Chemical composition may be determined by the measurement of a reaction product—in an automatic fashion utilizing the basic principles of conventional qualitative and quantitative chemical analysis. Two steps usually are involved in this type of instrumental analysis: (1) the formation of a target chemical reaction, and (2) the determination of one or more of the reaction products.

Determination of a constituent in a process stream or sample by measurement of a reaction product can be represented by: $C + R \rightarrow P$, where C = constituent to be determined; R = reactant; and P = reaction product to be measured. If reactant R already is present in the sample, it is only required to expose the sample to suitable reaction conditions to form P. Under normal instrument operating conditions, the reaction of C and R may be spontaneous. In other instances, suitable conditions may have to be established either (1) to promote the desired reaction (for example, setting the proper temperature and pressure, or using a catalyst) or (2) to assure a suitable reaction rate.

Frequently, it is possible to measure the reaction product as it forms in the reaction zone. In some instances, the products and sample residue must be removed from the reaction zone before a measurement can be made. Also, the reaction product may be measured directly; or its presence may have to be inferred from a secondary reaction. In one example, carbon monoxide in air or oxygen may be determined by combustion to carbon dioxide. The latter may be measured directly as by thermal-conductivity methods; or inferentially by absorbing the carbon dioxide in a solution and then measuring the change of that solution by electrolytic conductance.

ANALYZER (Reagent-Tape). The key to chemical analysis by this method is a tape (paper or fabric) that has been impregnated with a chemical substance that reacts with the unknown to form a reaction product on the tape which has some special characteristic, e.g., color, increased or decreased opacity, change in electrical conductance, or increased or lessened fluorescence. Small pieces of paper treated with lead acetate, for example, have been used manually by chemists for many years to determine the presence of hydrogen sulfide in a solution or in the atmosphere. This basic concept forms the foundation for a number of sophisticated instruments that may pretreat a sample gas, pass it over a cyclically advanced tape, and, for example, photo-metrically sense the color of the exposed tape, to establish a relationship between color and gas concentration. Depending upon the type of reaction involved, the tape may be wet or dry and it may be advanced continuously or periodically. Obviously, there are many possible variations within the framework of this general concept.

ANAMORPHISM. A term proposed by Van Hise in 1904 to designate the deep-seated constructive processes of metamorphism by which new complex (metamorphic) minerals are formed from the preexisting simpler minerals, as contrasted with the surface alteration of rocks due to weathering and cementation, termed katamorphism.

ANAPHYLAXIS. State of supersensitivity that may develop after a first injection of a foreign protein, such as a therapeutic or prophylactic serum. See also **Alkaloids**.

ANA-POSITION. The position of two substituent groups on atoms diagonally opposite, in α-positions on symmetrical fused rings, as the 1,5 or the 4,8 positions (which are identical) of the naphthalene ring.

ANATASE. The mineral anatase, TiO_2 crystallizing in the tetragonal system is a relatively uncommon mineral. It occurs as a tri-morphous form of TiO_2 with rutile and brookite. Rutile and anatase have tetragonal crystallization; brookite, orthorhombic. Hardness, 5.5–6; sp. gr. 3.82–3.97; brittle with sub-conchoidal fracture; color, shades of brown, into deep blue to black; also colorless, grayish, and greenish; also transparent to opaque with adamantine luster.

Anatase occurs as an accessory mineral in igneous and metamorphic rocks, gneisses, and schists. Fine crystals have been found in Arkansas in the United States, and in Switzerland.

ANDALUSITE. An aluminum silicate corresponding to the formula Al_2SiO_5, and is one of a three-member polymorphous group consisting of andalusite, sillimanite, and kyanite. Andalusite occurs in contact-metamorphic shales, and in rocks of regional metamorphic origin in association with sillimanite and kyanite. Andalusite crystallizes in the orthorhombic system, developing coarse prisms of approximately square cross section, but may be massive or granular. It shows a distinct cleavage parallel to the prism; hardness 6.5–7.5; sp. gr., 3.13–3.16; vitreous luster; colorless to white, gray, brown, greenish, or reddish; streak, white; transparent to opaque.

This mineral is named for its original locality, Andalusia, Spain. A variety of andalusite, chiastolite, has carbonaceous impurities so oriented that they produce a cross or a tesselated figure at right angles to the prism. Chiastolite comes from the Greek word meaning a cross. Localities are the Urals, the Alps, the Tyrol, the Pyrenees, Australia, and Brazil; in the United States, at Standish, Maine; Sterling and Lancaster, Massachusetts; Delaware County, Pennsylvania; and Madera County, California.

When clear it is used as a gemstone, and it has also been used to manufacture porcelain for spark plugs.

ANDESITE. A term originally applied to a porphyritic lava from the Andes Mountains by Leopold Van Buch. In modern terminology andesite is an extrusive igneous rock, the surface equivalent of diorite. In other words, it is composed chiefly of plagioclase, corresponding in chemical composition to oligoclase or andesine together, with biotite, hornblende, or pyroxene in varying quantities.

Andesites are of rather widespread occurrence, being found in the Rocky Mountains, California. Alaska, South America, and in many other localities.

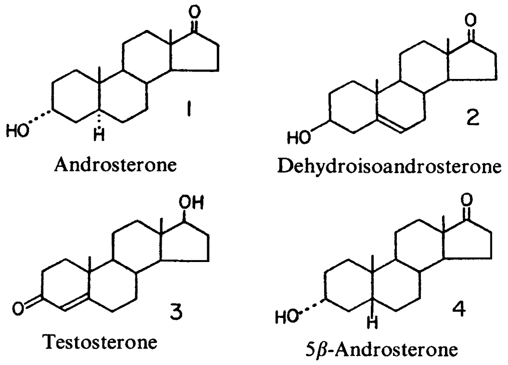
ANDROGENS. The relation between the testis and the male secondary sex characteristics has long been known. The evidence that a chemical substance present in the testis could elicit androgenic effects was not achieved until 1908 by Walker, who prepared an aqueous glycerol extract of bull testis tissue that caused growth of the capon's comb. More active extracts from bull testes were prepared in 1927 by McGee and Koch by using organic solvents. The extracts were assayed quantitatively by measuring the increase in area of the capon's comb. The discovery of androgenic activity in urine made possible the isolation of the first biologically active crystalline androgens by Butenandt et al. in 1931–1934. Androsterone and dehydroisoandrosterone were isolated from male urine. In 1935, David et al. isolated a crystalline hormone from bull testis extract. This possessed a higher biological activity than either androsterone or dehydroisoandrosterone. It was named testosterone. Testosterone was also prepared from cholesterol within months of its isolation from testular extract. See Fig. 1.

As pointed out by Liddle and Melmon (1974), adrenal androgen production also carried out in the *zona fasciculata* and in the *zona reticularis*, varies greatly at different stages of life. The fetus makes significant amounts of adrenal androgen, whereas the child makes very little. Beginning with puberty, adrenal androgen production increases, reaches a peak in early adulthood, and then declines to rather low levels beyond age 50. On the other hand, the secretion of ACTH, the only known control of adrenal androgen biosynthesis, shows no age-related fluctuations. The full regulation of adrenal androgen production is not understood. Adrenal androgens are relatively weak, but some serve as precursors for hepatic conversion to testosterone. Hyperfunction of this pathway in the female may lead to significant masculinization. See also **Adrenal Cortical Hormones**; and **Adrenal Medulla Hormones**.

The androgens stimulate the development of the male secondary structures, such as the penis, scrotum, seminal vesicles, prostate gland, vas deferens and epididymis. The deepening of the voice, the growth of pubic, axillary, body, and facial hair, as well as the development of the characteristic musculature of the human male, are also under the influence of testosterone. If the testes fail to develop or are removed prior to puberty, these changes do not occur. Thus, testosterone is essential for reproductive function of the male.

The adrenal cortex produces hydroisoandrosterone, which is largely found in blood and urine conjugated as the sulfate ester. The amounts of androgen secreted by the normal adrenal cortex are insufficient to maintain reproductive function in the male. The normal human ovary and placenta also produce small amounts of androgenic steroids that serve as precursors for the estrogens in these tissues. In the human, little testosterone is excreted into the urine and virtually none into the feces. The principal metabolic transformation products are androsterone and 5β-androsterone, with small amounts of other reduced compounds. These substances are excreted in the urine in the form of esters with sulfuric acid or glycosides with glucuronic acid.

Like all other classes of steroid hormones, the androgens are synthesized from acetyl coenzyme A *via* mevalonic acid, isopentenyl pyrophosphate, farnesyl pyrophosphate, squalene, lanosterol, and cholesterol. Enzyme



Androsterone

Dehydroisoandrosterone

Testosterone

5β-Androsterone

Fig. 1. Androsterone and related hormones

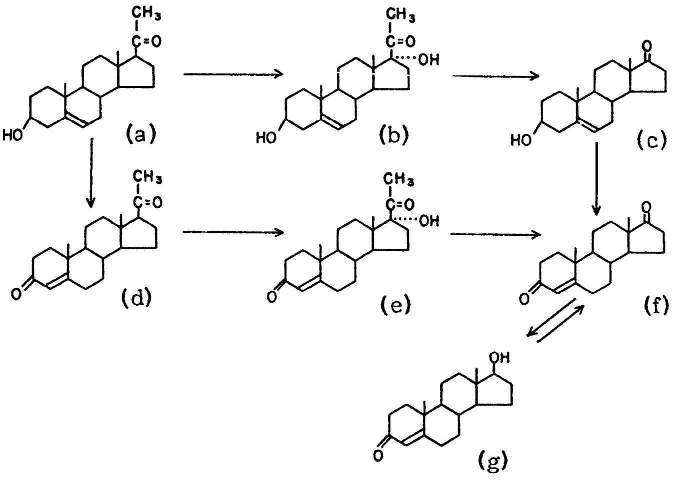


Fig. 2. Biosynthesis of testosterone: **(a)** Pregnenolone; **(b)** 17-hydroxy pregnenoline; **(c)** dehydroisoandrosterone; **(d)** progesterone; **(e)** 17-hydroxypro ges terone; **(f)** androstenedione; **(g)** testosterone

systems in the testis then catalyze the cleavage of the side chain of cholesterol to pregnenolone which can give rise to testosterone by the two pathways shown in Fig. 2.

Testosterone is formed by the interstitial or Leydig cells of the testes which develop under the influence of gonadotrophic hormones discharged into the bloodstream by the anterior pituitary gland. In pituitary insufficiency, this hormonal stimulus is lacking and, as a consequence, the Leydig cells do not secrete testosterone. In such instances, the male secondary sex characteristics fail to develop. However, interstitial cell tumors may occur, leading to excessive androgen production and precocious puberty. In women, tumors or excessive function of the adrenal cortex and, rarely, of the ovary, result in the production of large amounts of androgens with associated virilization.

Acne vulgaris, a chronic skin disorder, is related to androgen production. The post-pubescent development of the sebaceous glands and the onset of acne are dependent upon the presence of androgens, but are not related to testosterone blood levels. Sansone et al. (1971) observed that the hypothesis of increased end-organ sensitivity, which is supported by the heightened ability of skin with acne to metabolize testosterone, may explain the lack of correlation between levels of circulating androgens and occurrence and severity of the disease.

There is androgen involvement in polycystic ovary syndrome (PCO) and hyperthecosis. In 1935, Stein and Leventhal defined a condition with hirsutism, secondary amenorrhea, and enlarged ovaries—a syndrome now referred to as PCO. In this condition, the female usually shows signs of androgen excess, including increased body hair, but true virilism, with balding and deepening of the voice, is less common. Usually, one or both ovaries are enlarged. In many patients the ovaries are cystic, with thickened capsules, yet not palpably enlarged. It has been postulated that the development of PCO commences when luteinizing hormone (LH) triggers an increase in ovarian androgen, which is converted to estrogen, causing estrogen levels (particularly estrone) to increase. This is followed by an anterior pituitary response to luteinizing hormone-releasing hormone (LRH). This completes the cycle by creating exaggerated pulsatile but surgeless LH levels. The initiating lesion remains obscure. Wedge resection of one or both ovaries has largely been replaced by the administration of the antiestrogen clomiphene. This was the first drug known to trigger ovulation in women. Patients with anovulation arising from PCO are treated with the drug primarily when fertility is desired. The hirsutism found with PCO has been difficult to treat. Wood and Boronow (1976) reported that long intervals of anovulation, such as occur in PCO, may be a prelude to endometrial carcinoma. As postulated, the link may either be continuous exposure of the endometrium to estrogen unopposed by progesterone. There is also the postulation that estrone, the estrogen that appears to be high in this disorder, may be a causative factor. A carcinogenic role has been alleged for estrone.

In a somewhat related disorder, hyperthecosis, androgen excess tends to be greater. In this condition, there is prominent luteinization of the theca, whereas the cystic development and capsular thickening of the PCO are absent. Ovarian tumors making androgen can produce the features of PCO, but they tend to have a course with sharper onset and clearer progression.

Androgens also have been used in the management and treatment of agnogenic myeloid metaplasia, aplastic anemia, breast cancer, hereditary angiodema, osteoporosis, paroxysmal nocturnal hemoglobinuria, and sideroblastic anemia.

Oral androgens as may be used in hormone therapy for the management of metastatic breast cancer are effective in about 30% of women regardless of age, but virilizing doses of the hormone are usually required. The oral androgens carry the additional risk of toxic hepatitis.

Androgens may explain some of the differences between heart diseases of males and females.

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ANDROSTERONE. See **Steroids**.

ANESTHETICS. The term anesthesia comes from the Greek *anaisthai* or insensibility and constitutes a state in which perception of noxious events such as surgical procedures is imperceptible. This state may or may not be accompanied by loss of consciousness. A complete or general anesthetic given by the inhalation or intravenous routes produces hypnosis (profound sleep), analgesia, muscle relaxation, and protection against the increase in blood pressure and heart rate resulting from surgical stress (maintains homeostasis). An anesthetic which blocks the neural transmission of painful stimuli through afferent nerves and does not affect the level of consciousness can be classified as a local anesthetic.

The induction of general anesthesia produces a progressive deepening of the anesthetic state and represents, in the anatomical sense, a descending desensitization of the central nervous system (CNS). A progression of clinical signs are useful for estimating the depth of anesthesia. These signs vary somewhat for each anesthetic, but in general four stages can be defined: *(1)* state of altered consciousness and analgesia indicative of action on cerebral canticle areas begin; *(2)* loss of consciousness, often accompanied by delirium and excitement, occurs. Irregular respiration and motor movement result from depression of higher motor inhibitory centers with the release of lower motor mechanisms; *(3)* stage of surgical anesthesia is reached in which spinal cord and spinal reflexes are abolished, providing relaxation of skeletal musculature. Within the four planes in this state are loss of corneal, conjunctival, pharyngeal, and laryngeal reflexes as the depth of anesthesia progresses; *(4)* onset of respiratory paralysis occurs resulting from significant depression of the medullary respiratory center. Subsequent cardiovascular collapse ensues.

Most signs which require a skeletal muscle reflex would not be apparent after treatment with a neuromuscular blocking drug or would be altered significantly by preoperative drugs. In these cases central nervous system monitoring via an electroencephalogram (EEG), and hemodynamic and blood gas monitoring, help assess the depth of anesthesia. The potency of inhaled agents is expressed as the minimum alveolar concentration (MAC) that is required to prevent spontaneous movement in response to a surgical or equivalent stimulus in 50% of patients.

The onset of action is fast (within 60 s) for the intravenous anesthetic agents and somewhat slower for inhalation and local anesthetics. The induction time for inhalation agents is a function of the equilibrium established between the alveolar concentration relative to the inspired concentration of the gas. Onset of anesthesia can be enhanced by increasing the inspired concentration to approximately twice the desired alveolar concentration, then reducing the concentration once induction is achieved. The onset of local anesthetic action is influenced by the site, route, dosage (volume and concentration), and pH at the injection site.

Theories of General Anesthesia

Although the modern practice of anesthesia is exceedingly sophisticated, identification of the basic molecular mechanism underlying it is still lacking. Even whether the target sites of the inhalational anesthetics are lipid or protein remains unknown, although it is likely that proteins are intimately involved. The inhalational anesthetics are very diverse chemically and extrapolation from the effect of a particular agent to the physiological state of anesthesia is problematic. However, anesthesia theories may be roughly divided into two categories: lipid theories and protein theories.

Lipid Theories. Although there are many varieties of the lipid theory all postulate that inhalational anesthetics exert their primary effects by dissolving in the lipid portions of nerves, thereby altering the conductivity. The primary site of action is postulated to be the lipid matrix of cell membranes.

Protein Theories. The direct interaction of inhalation anesthetics and proteins has been proposed as the cause of anesthesia. An inhalation agent, whether a noble gas or a fluorinated ether, could dissolve asymmetrically in a protein. Resultant conformational changes in the protein, if these changes occur, could then cause changes in biological activity.

Anesthetic Agents

Inhalation Agents. An ideal inhalation anesthetic would exhibit physical, chemical, and pharmacological properties allowing safe usage in a variety of surgical interventions. The agent should be odorless, nonflammable at concentrations which are likely to be used in the operating room, and stable both on storage and to soda lime, which is used as the CO_2 absorber in the anesthetic circuit. Induction of, and recovery from, anesthesia should be rapid, and minimal side effects should be observed on the cardiovascular (depression and epinephrine compatibility) or central nervous systems (EEG activation). See also **Neuroregulators**. The drug should not be metabolized.

A number of inhalation anesthetics have been introduced to clinical practice, some of which are listed in Table 1. All agents introduced after 1950, except ethyl vinyl ether, contain fluorine. Agents such as ether, chloroform, trichloroethylene (Trilene), cyclopropane, and fluoroxene (Fluoromar), which were once used, have been displaced by the newer fluorinated anesthetics.

Intravenous Anesthetic. The intravenous (iv) anesthetic agents are of two types: those which are used to induce, but not maintain, anesthesia, and those which are useful not only for induction, but also for maintenance. The period of induction is perhaps the most crucial part of the anesthesia. The need is for an anesthetic agent having an extremely fast rate of onset and limited side effects. Fast onset minimizes the stress and agitation which could arise during a more lengthy induction. Various classes of compounds have been used. Among these are: barbiturates, opioids, steroids, benzodiazepines, and hindered phenols. But the ideal agent for both induction and maintenance has not yet been found. For this reason, balanced anesthesia is often used: a potent opioid is combined with an inhalation agent.

A major difference between the inhalational agents and the iv anesthetics is that the former probably exert their biological activity through physical effects while the latter, in most cases, function through a biological receptor-mediated pathway.

TABLE 1. PROPERTIES AND PARTITION COEFFICIENTS OF INHALATION ANESTHETICS

Agent	Molecular formula	Partition coefficient Oil/gas	Blood/gas	Boiling point, °C	Year introduced
ethyl ether	$C_4H_{10}O$	65	12.1	35	1842
chloroform	$CHCl_3$	394	8.4	61	1847
trichloroethylene	C_2HCl_3	200–250	9.0	87	1934
fluoroxene	$C_4H_5F_3O$	47	1.37	43.1	1960
halothane	$C_2HBrClF_3$	224	2.3	50.2	1956
isoflurane	$C_3H_2ClF_5O$	90.8	1.4	48.5	1980
enflurane	$C_3H_2ClF_5O$	96.5	1.9	56.5	1972
methoxyflurane	$C_3H_4Cl_2F_2O$	970	12.0	105	1962
sevoflurane	$C_4H_3F_7O$	42	0.6	58	1989
desflurane	$C_3H_2F_6O$	18.7	0.42	23.5	
nitrous oxide	N_2O	1.4	0.46	−89.5	1850s
cyclopropane	C_3H_6			−33	1934

Opioid Reversal Agents. At the end of a surgery, when the decision is made to reverse opioid-induced activity, the primary concern is to eliminate the respiratory depressant effects inherent in the potent opiates used as anesthetics. This reversal, brought about by opioid reversal agents, can also diminish the analgesic effects of the opiates. There are two types of reversal agents: pure antagonists and mixed agonist–antagonists. The antagonists naloxone and naltrexone are the most commonly used, although the use of the agonist–antagonist nalbuphine is increasing because it maintains a moderate level of analgesia while reversing the side effects. Nalmefene, a long-acting reversal agent, is in clinical trials.

Local Anesthetics. Nerve impulses are initiated by membrane depolarization, effected by the opening of a sodium-ion channel and an influx of sodium ions. Local anesthetics act by inhibiting the channel's opening; they bind to a receptor located in the channel's interior. The degree of blockage on an isolated nerve depends not only on the amount of drug, but also on the rate of nerve stimulation.

Local anesthetic activity is usually demonstrated by compounds which possess both an aromatic and an amine moiety separated by a lipophilic hydrocarbon chain and a polar group. In the clinically useful agents (Table 2) the polar group is an ester or an amide. Activity may be maintained, however, when the polar function is an ether, thioether, ketone, or thioester.

Pharmacological Profile. The profile of the ideal local anesthetic agent depends largely on the type and length of the surgical procedure for which it is applied. Procedures could include neuraxial (spinal and epidural) anesthesia, nerve and plexus blocks, or field blocks (local infiltration). In general, the ideal agent should have a short onset of anesthesia and be useful for multiple indications such as infiltration, nerve blocks,

TABLE 2. CLINICALLY USED LOCAL ANESTHETIC AGENTS

Agent	Method of application	Comment
	Amino esters	
procaine	infiltration, spinal	slow onset, short duration
chloroprocaine	peripheral nerve and obstetric extradural	fast onset, short duration, low systemic toxicity
tetracaine	spinal	slow onset, long duration, high systemic toxicity
	Amino amides	
lidocaine	infiltration, iv regional, peripheral nerve block, extradural block, spinal and topical	fast onset, moderate duration, low systemic toxicity, most versatile agent
mepivacaine	infiltration, peripheral nerve block, extradural	similar to lidocaine
prilocaine	similar to lidocaine	safest amino amide, methemoglobinemia at high doses
bupivacaine	infiltration, peripheral nerve block, extradural	moderate onset, long duration, potential for cardiovascular side effects, sensory/motor separation
etidocaine	infiltration, peripheral nerve block, extradural	fast onset, long duration, profound motor block

intravenous, extradural, spinal, and topical administration. The therapeutic indexes for systemic CNS and cardiovascular toxicity should be high and the agent should be compatible with the vasoconstrictor epinephrine.

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Anaquest

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ANFINSEN, CHRISTIAN B. (1916–1995). An American biochemist who won the Nobel prize for chemistry in 1972 for his work on ribonuclease, especially concerning the connection between the amino acid sequence and the biologically active conformation. He shared the Nobel prize with Stanford Moore and William H. Stein. His doctorate was granted from Harvard.

ANGLESITE. Naturally occurring lead sulfate ($PbSO_4$), which crystallizes in the orthorhombic system and may be found mixed with galena, from which it is usually formed by oxidation. Hardness, 3; specific gravity, 6.12–6.39; luster, adamantine to vitreous or resinous; transparent to opaque; streak, white; colorless to white or green, but rarely may be yellow or blue. This mineral is used as a source of lead.

Anglesite, whose name derives from Anglesey, England, is found in many European localities; in the United States it has been found in large crystals in the Wheatley Mine, Phoenixville, Pennsylvania, and also in Missouri, Utah, Arizona, and Idaho.

ÅNGSTROM (Å). A unit of length almost one non-hundred millionth (10^{-8}) centimeter. The Ångstrom is defined in terms of the wavelength of the red line of cadmium (6438.4696 Å). Used in stating distances between atoms, dimensions of molecules, wavelengths of short-wave radiation, etc.

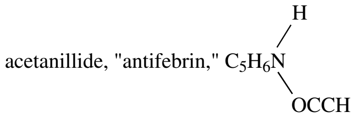
ANHYDRIDE. A chemical compound derived from and acid by elimination of a molecule of water. Thus sulfur trioxide, SO_3, is the anhydride of sulfuric acid; CO_2 is the anhydride of carbonic acid; phthalic acid, $C_6H_4(CO_2H)_2$ minus water gives phthalic anhydride. The term should not be confused with *anhydrous*.

ANHYDRITE. The mineral anhydrous calcium sulfate, $CaSO_4$, occurs in granular, scaly, or fibrous masses, is rarely crystallized in orthorhombic tabular or prismatic forms. Hardness, 3–3.5; sp gr, 2.9–2.98; translucent to opaque; streak white; color, white, gray, bluish, or reddish. Anhydrite has three cleavages at right angles to one another. It is similar to gypsum and occurs under the same conditions, often with the latter mineral. It is usually found in sedimentary rocks associated with limestones, salt, and gypsum, into which it changes slowly by the absorption of water. See also **Gypsum**.

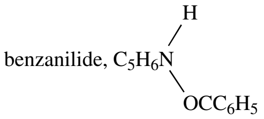
Anhydrite is found in Poland, Saxony, Bavaria, Württemberg, Switzerland, and France; in the United States, in South Dakota, New Mexico, Texas, New Jersey, and Massachusetts; in Canada, in Nova Scotia, New Brunswick, and exceptional specimens from the Faraday Uranium Mine near Bancroft, Ontario.

ANHYDROUS. Descriptive of an inorganic compound that does not contain water either adsorbed on its surface or combined as water of crystallization. Do not confuse with *anhydride*.

ANILINE. Aniline, phenylamine, aminobenzene, $C_6H_5NH_2$, is a colorless, odorous liquid, an amine, with melting point−6°C, boiling point 184°C, is slightly soluble in water, miscible in all proportions with alcohol or ether, poisonous, turns yellow to brown in the air, is a weak base forming salts with acids, e.g., anilinehydrochloride ("aniline salt," $C_6H_5NH_2 \cdot HCl$) from which aniline is reformed by addition of sodium hydroxide solution. Aniline reacts (1) with hypochlorite solution, to form a transient violet coloration, (2) with nitrous acid (a) warm, to form nitrogen gas plus phenol, (b) cold, to form diazonium salt (benzene diazonium chloride, $C_6H_5N{-}Cl$), (3) with acetyl chloride, acetic anhydride, or acetic acid glacial, to form N-phenylacetamide


acetanillide, "antifebrin," $$C_5H_6\overset{H\,/}{\underset{\backslash\,OCCH_3}{N}}$$

(4) with benzoyl chloride, to form N-phenylbenzamide


benzanilide, $$C_5H_6\overset{H\,/}{\underset{\backslash\,OCC_6H_5}{N}}$$

(5) with benzenesulfonyl chloride, to form N-phenylbenzene sulfonamide, $C_6H_5SO_2NHC_6H_5$, soluble in sodium hydroxide, (6) with chloroform, $CHCl_3$, plus alcohol plus sodium hydroxide, to form phenyl isocyanide, C_6H_5NC, very poisonous, (7) with H_2SO_4 at 180° to 200°C, to form para -aminobenzene sulfonic acid (sulfanilic acid, $H_2N \cdot C_6H_4 \cdot SO_2H$ (1,4)), (8) with HNO_3, when the amine group is protected, e.g., using acetanilide, to form mainly paranitroacetanilide, $CH_3CONH \cdot C_6H_4 \cdot NO_2$ (1.4), from which paranitroaniline, $H_2N{\cdot}C_6H_4{\cdot}NO_2(1{,}4)$ is obtained by boiling with concentrated hydrochloric acid, (9) with chlorine in an anhydrous solvent, such as chloroform or acetic acid glacial, to form 2,4,6-trichloroaniline (1) $H_2N \cdot C_6H_2Cl_3(2{,}4{,}6)$, (10) with bromine water, to form white solid 2,4,6-tribromoaniline, (1)$H_2N \cdot C_6H_2Br_3(2{,}4{,}6)$, (11) with potassium dichromate in sulfuric acid, to form aniline black dye, and, by further oxidation, benzoquinone, $O{:}C_6H_4{:}O$ (1,4), (12) with potassium permanganate in sodium hydroxide, to form azobenzene, $C_6H_5N{:}NC_6H_5$, along with some azoxybenzene $C_6H_5NO{:}NC_6H_5$, (13) with reducing agents, to form aminohexahydrobenzene (cyclohexylamine, $H_2N \cdot C_6H_{11}$), (14) with alkyl halides or alcohols heated, to form alkyl anilines, e.g., methylaniline, $C_6H_5NHCH_3$, dimethylaniline, $C_6H_5N(CH_3)_2$.

Aniline may be made (1) by the reduction, with iron or tin in HCl, of nitrobenzene, and (2) by the amination of chlorobenzene by heating with ammonia to a high temperature corresponding to a pressure of over 200 atmospheres in the presence of a catalyst (a mixture of cuprous chloride and oxide). Aniline is the end-point of reduction of most mono-nitrogen substituted benzene nuclei, as nitrosobenzene, beta-phenylhydroxylamine, azoxybenzene, azobenzene, hydrazobenzene. Aniline is detected by the violet coloration produced by a small amount of sodium hypochlorite.

Aniline is used (1) as a solvent, (2) in the preparation of compounds as illustrated above, (3) in the manufacture of dyes and their intermediates, (4) in the manufacture of medicinal chemicals. See also **Amines**.

ANION. A negatively-charged atom or radical. In electrolysis, an anion is the ion which deposits on the anode; that portion of an electrolyte which carries the negative charge and travels against the conventional direction of the electric current in a cell. Within the category of anions are included the nonmetallic ions and the acid radicals, as well as the hydroxyl ion, OH^-. In electrochemical reactions, they are designated by the minus sign placed above and after the symbol, such as Cl^- and $SO_4{}^{2-}$, the number of the minus sign indicating the magnitude, in electrons, of the electrical charge carried by the anion. In a battery, it is the deposition of negative anions that makes the anode negative. See also **Ion**.