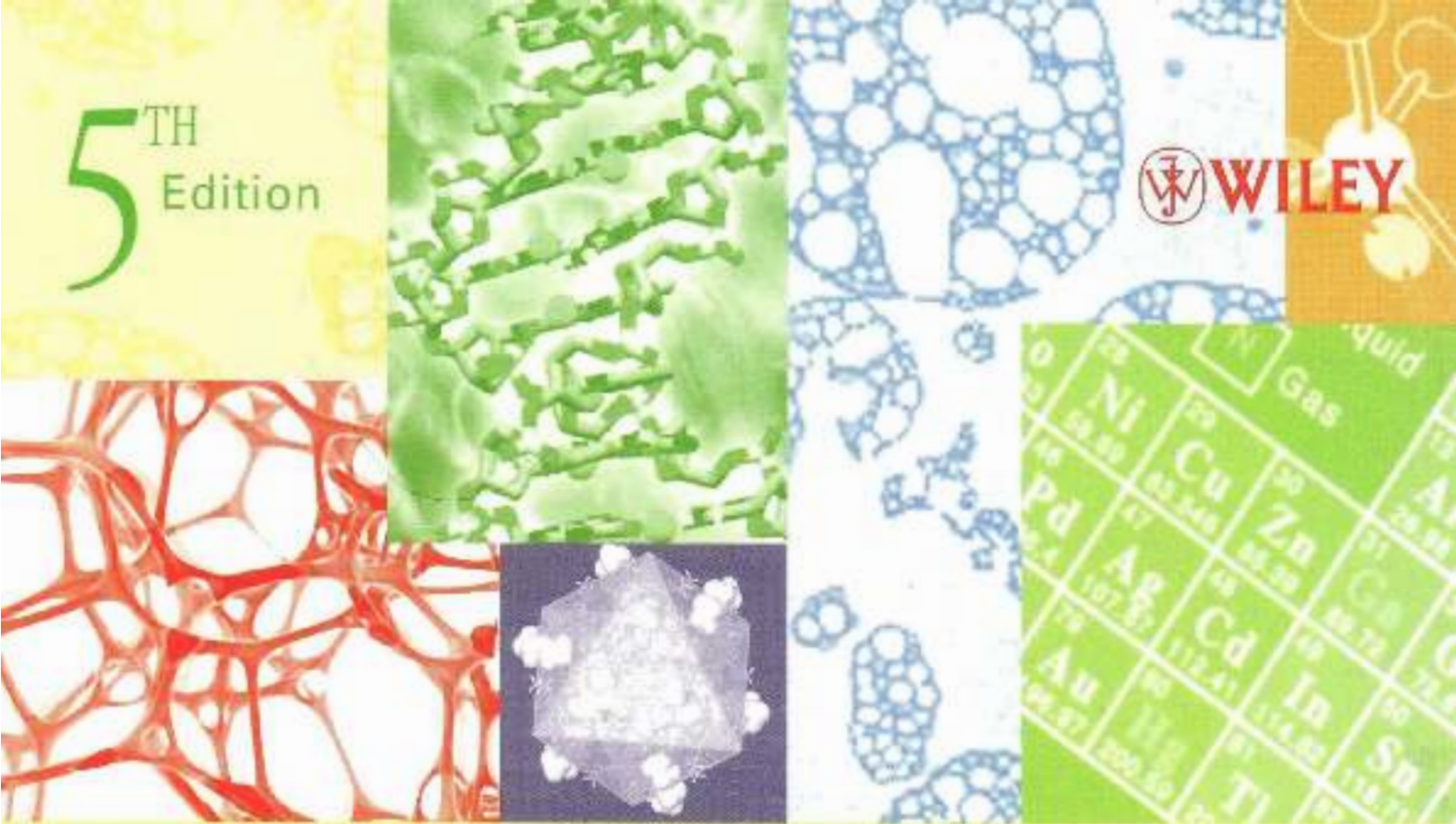


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Edition

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*Van Nostrand's*

# ENCYCLOPEDIA *of* CHEMISTRY



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Editor-in-Chief

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<sup>2</sup> <b>He</b> helium 4.003	<sup>10</sup> <b>Ne</b> neon 20.18	<sup>18</sup> <b>Ar</b> argon 39.95	<sup>36</sup> <b>Kr</b> krypton 83.80	<sup>54</sup> <b>Xc</b> xenon 131.3	<sup>86</sup> <b>Rn</b> radon 222	<sup>118</sup> <b>Uuo</b> ununoctium (223)
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# 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 pyrolyzed 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 <sup>a</sup>
Kaolinite	5, 6, 7	5.5 <sup>a</sup>
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 <sup>a</sup>
Labradorite		8.0 9.2 <sup>a</sup>
Albite	9, 10	
Dolomite	9, 10	8.5
Hornblende	10	8.9
Leucite	10	
Diopside	10, 11	9.9
Olivine	10, 11	9.6 <sup>a</sup>
Magnesite	10, 11	

<sup>a</sup> More recent values published in literature.



### Additional Reading

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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 <sup>a</sup> , kN/m <sup>2b</sup>
talc	1			
calcite	3			
apatite	5			
vitreous silica		7		
topaz	8	9		13
corundum	9		9	20
fused ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>				16
SiC		13	14	24
cubic boron nitride				46
diamond	10	15	42.5	78

<sup>a</sup>At a 100-g load (K-100) average.

<sup>b</sup>To convert kN/m<sup>2</sup> to kgf/mm<sup>2</sup> divide by 0.00981.

<sup>c</sup>39% ZrO<sub>2</sub> (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  $\alpha$ -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  $-273.15^{\circ}\text{C}$ , on the Fahrenheit scale,  $-459.67^{\circ}\text{F}$ ; 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,  $Q_2$ . If  $Q_1$  is the heat exhausted from the engine,

$$E = (W/Q_2) = (Q_2 - Q_1)/Q_2 = 1 - (Q_1/Q_2)$$

where  $W$ ,  $Q_1$ , and  $Q_2$  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  $Q_1/Q_2$  must depend only on the two temperatures and on nothing else. The Kelvin temperatures are then defined by the relation where  $Q_1/Q_2$  is the ratio of the heats rejected and absorbed, and  $T_1/T_2$  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.

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

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

## 4 ABSORPTION (Process)

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 1/4 inch (6 millimeters) up to 2 inches (5 centimeters); raschig rings range from 1/4 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 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.

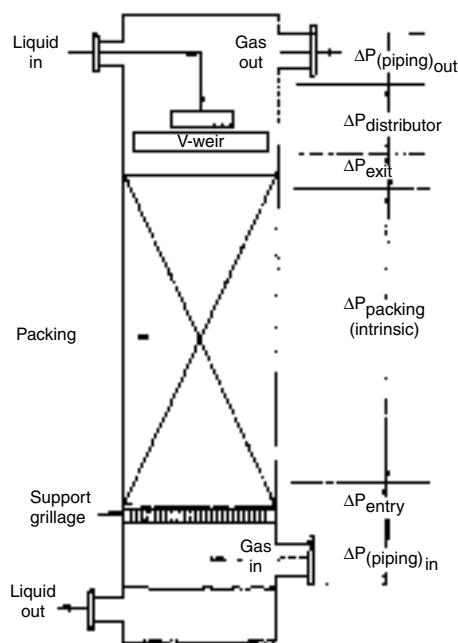


Fig. 1. Section of representative packed absorption tower

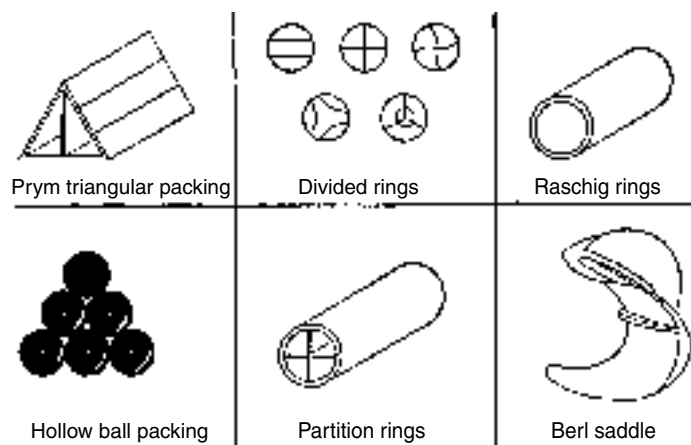


Fig. 2. Types of packing used in absorption towers

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  $\gamma$  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 processes 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 <sub>2</sub>	55	(2) Al <sub>2</sub> O <sub>3</sub>	15	(3) CaCO <sub>3</sub>	8.8
(4) MgO	1.6	(5) Na <sub>2</sub> O	1.6	(6) K <sub>2</sub> O	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.

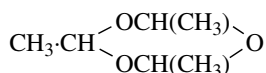
2. A compound added to a photographic developer to increase its activity, such as certain quaternary ammonium compounds and alkaline substances.

3. A particle accelerator.

**ACETALDEHYDE.** [CAS: 75-07-0]. CH<sub>3</sub>CHO, 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<sub>2</sub>O, 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<sub>3</sub>CHO)<sub>3</sub> 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  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{NH}_2$ , white solid, mp  $97^\circ\text{C}$ , bp  $111^\circ\text{C}$ , with decomposition, (6) with concentrated  $\text{H}_2\text{SO}_4$ , heat is evolved, and with rise of temperature, paraldehyde  $(\text{C}_2\text{H}_4\text{O})_3$  or



colorless liquid bp  $124^\circ\text{C}$ , slightly soluble in  $\text{H}_2\text{O}$ , is formed, (7) with acids, below  $0^\circ\text{C}$ , forms metaldehyde  $(\text{C}_2\text{H}_4\text{O})_x$ , white solid, sublimes at about  $115^\circ\text{C}$  without melting but with partial conversion to acetaldehyde, (8) with dilute HCl or dilute NaOH, aldol,  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CH}_2\text{CHO}$  slowly forms, (9) with phosphorus pentachloride, forms ethylidene chloride,  $\text{CH}_3 \cdot \text{CHCl}_2$ , colorless liquid, bp  $58^\circ\text{C}$ , (10) with ethyl alcohol and dry hydrogen chloride, forms acetal, 1,1-diethoxyethane  $\text{CH}_3 \cdot \text{CH}(\text{OC}_2\text{H}_5)_2$ , colorless liquid, bp  $104^\circ\text{C}$ , (11) with hydrocyanic acid, forms acetaldehyde cyanohydrin,  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{CN}$ , readily converted into alpha-hydroxypropionic acid,  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{COOH}$ , (12) with sodium hydrogen sulfite, forms acetaldehyde sodium bisulfite,  $\text{CH}_3 \cdot \text{CHOH} \cdot \text{SO}_3\text{Na}$ , white solid, from which acetaldehyde is readily recoverable by treatment with sodium carbonate solution, (13) with hydroxylamine hydrochloride forms acetaldoxime,  $\text{CH}_3 \cdot \text{CH}:\text{NOH}$ , white solid, mp  $47^\circ\text{C}$ , (14) with phenylhydrazine, forms acetaldehyde phenylhydrazone,  $\text{CH}_3 \cdot \text{CH}:\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , white solid, mp  $98^\circ\text{C}$ , (15) with magnesium methyl iodide in anhydrous ether ("Grignard's solution"), yields, after reaction with water, isopropyl alcohol,  $(\text{CH}_3)_2\text{CHOH}$ , a secondary alcohol, (16) with semicarbazide, forms acetaldehyde semicarbazone,  $\text{CH}_3 \cdot \text{CH}:\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , white solid, mp  $162^\circ\text{C}$ , (17) with chlorine, forms trichloroacetaldehyde ("chloral"),  $\text{CCl}_3 \cdot \text{CHO}$ , (18) with  $\text{H}_2\text{S}$ , forms thioacetaldehyde,  $\text{CH}_3 \cdot \text{CHS}$  or  $(\text{CH}_3 \cdot \text{CHS})_3$ . 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 catalyst, 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  $\text{H}_2\text{SO}_4$  (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  $\text{RCH}(\text{OR}')(\text{OR}'')$  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  $\text{H}_2\text{O}$ , and generally are similar structurally to ethers. Unlike ethers, acetals are hydrolyzed by acids into their respective aldehydes.  $\text{H}(\text{R})\text{CO} + (\text{HO} \cdot \text{C}_2\text{H}_5)_2 \longrightarrow \text{H}(\text{R})\text{C}(\text{OC}_2\text{H}_5)_2 + \text{H}_2\text{O}$ . Representative acetals include:  $\text{CH}_2(\text{OCH}_3)_2$ , methylene dimethyl ether, bp  $42^\circ\text{C}$ ;  $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ , ethylidene dimethyl ether, bp  $64^\circ\text{C}$ ; and  $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ , ethylidene diethyl ether, bp  $104^\circ\text{C}$ .

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

**ACETATE DYE.** One group comprises water insoluble azo or anthraquinone dyes that have been 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].  $\text{CH}_3\text{COOH}$ , formula weight 60.05, colorless, acrid liquid, mp  $16.7^\circ\text{C}$ , bp  $118.1^\circ\text{C}$ , sp gr 1.049. Also known as ethanoic acid or vinegar acid, this compound is miscible with  $\text{H}_2\text{O}$ , alcohol, and ether in all proportions. Acetic acid is available commercially in several concentrations. The  $\text{CH}_3\text{COOH}$  content of glacial acetic is approximately 99.7% with  $\text{H}_2\text{O}$ , the principal impurity. Reagent acetic acid generally contains 36%  $\text{CH}_3\text{COOH}$  by weight. Standard commercial aqueous solutions are 28, 56, 70, 80, 85, and 90%  $\text{CH}_3\text{COOH}$ . Acetic acid is the active ingredient in vinegar in which the content ranges from 4 to 5%  $\text{CH}_3\text{COOH}$ . 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:  $\text{C}_2\text{H}_5\text{OH} + \text{O}_2 \longrightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$ , 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  $250^\circ\text{C}$ . The reaction takes place in the liquid phase and dissolved cobaltous iodide is the catalyst.  $\text{CH}_3\text{OH} + \text{CO} \longrightarrow \text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} + 2\text{CO} \longrightarrow 2\text{CH}_3\text{COOH}$ . 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  $\text{CH}_3\text{COOH}$ .

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  $\text{CH}_3\text{CO}\cdot\text{Cl}$ , which is an important reagent for transfer of the acetyl ( $\text{CH}_3\text{CO}\cdot$ ) 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%  $\text{La}(\text{NO}_3)_3$  solution, a drop of 0.01-N iodine solution, and a drop of 0.1%  $\text{NH}_4\text{OH}$  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  $\text{H}_2\text{SO}_4$  are added to the acetate solution and warmed to form a colorless solution.

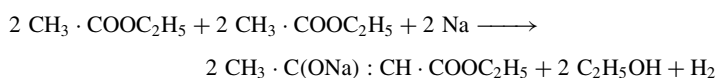
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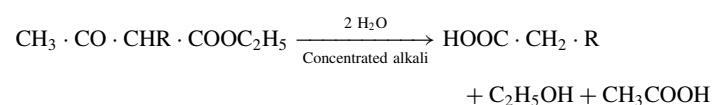
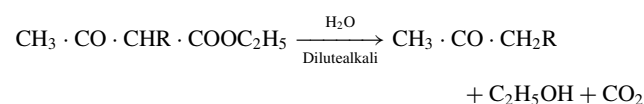
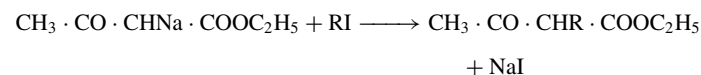
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**ACETOACTETIC ESTER CONDENSATION.** A class of reactions occasioned by the dehydrating power of metallic sodium or sodium ethoxide on the ethyl esters of monobasic aliphatic acids and a few other esters. It is best known in the formation of acetoacetic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



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 ( $\text{CH}_3 \cdot \text{COH} : \text{CH} \cdot \text{COOC}_2\text{H}_5$  and  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ ).

On boiling ester with acids or alkalis 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 alkalis, 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  $\cdot \text{CH}_2 \cdot$  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.



**ACETONE.** [CAS: 67-64-1].  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ , formula weight 58.08, colorless, odorous liquid ketone, mp  $-94.6^\circ\text{C}$ , bp  $56.5^\circ\text{C}$ , sp gr 0.792. Also known as dimethyl ketone or propanone, this compound is miscible in all proportions with  $\text{H}_2\text{O}$ , 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)  $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COH}(\text{CH}_3)_2$  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  $-54^\circ\text{C}$ , bp  $166^\circ\text{C}$ , 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:



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:  $\text{CH}_3\text{CH} = \text{CH}_2 + 1/2 \text{O}_2 \longrightarrow \text{CH}_3\text{COCH}_3$ . 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  $100^\circ\text{C}$ .

Acetone reacts with many chemicals in a marked manner: (1) with phosphorus pentachloride, yields acetone chloride  $(\text{CH}_3)_2\text{CCl}_2$ , (2) with hydrogen chloride dry, yields both mesityl oxide  $\text{CH}_3\text{COCH} : \text{C}(\text{CH}_3)_2$ , liquid, bp  $132^\circ\text{C}$ , and phorone  $(\text{CH}_3)_2\text{C} : \text{CHCOCH} : \text{C}(\text{CH}_3)_2$ , yellow solid, mp  $28^\circ\text{C}$ , (3) with concentrated  $\text{H}_2\text{SO}_4$ , yields mesitylene  $\text{C}_6\text{H}_3(\text{CH}_3)_3$  (1,3,5), (4) with  $\text{NH}_3$ , yields acetone amines, e.g., diacetoneamine  $\text{C}_6\text{H}_{12}\text{ONH}$ , (5) with HCN, yields acetone cyanohydrin  $(\text{CH}_3)_2\text{CHOH} \cdot \text{CN}$ , readily converted into alpha-hydroxy acid  $(\text{CH}_3)_2\text{CHOH} \cdot \text{COOH}$ , (6) with sodium hydrogen sulfite, forms acetone-sodiumbisulfite  $(\text{CH}_3)_2 \text{COH} \cdot \text{SO}_3\text{Na}$  white solid, from which acetone is readily recoverable by treatment with sodium carbonate solution, (7) with hydroxylamine hydrochloride, forms acetoxime  $(\text{CH}_3)_2\text{C} : \text{NOH}$ , solid, mp  $60^\circ\text{C}$ , (8) with phenylhydrazine, yields acetonephenyl-hydrazone  $(\text{CH}_3)_2\text{C} : \text{NNHC}_6\text{H}_5 \cdot \text{H}_2\text{O}$ , solid, mp  $16^\circ\text{C}$ , anhydrous compound, mp  $42^\circ\text{C}$ , (9) with semicarbazide, forms acetonesemicarbazone  $(\text{CH}_3)_2\text{C} : \text{NNHCONH}_2$ , solid, mp  $189^\circ\text{C}$ , (10) with magnesium methyl iodide in anhydrous ether ("Grignard's solution"), yields, after reaction with  $\text{H}_2\text{O}$ , trimethylcarbinol  $(\text{CH}_3)_3\text{COH}$ , a tertiary alcohol, (11) with ethyl thioalcohol and hydrogen chloride dry, yields mercaptol  $(\text{CH}_3)_2\text{C}(\text{SC}_2\text{H}_5)_2$ , (12) with hypochlorite, hypobromite, or hypiodite solution, yields chloroform  $\text{CHCl}_3$ , bromoform  $\text{CHBr}_3$  or iodoform  $\text{CHI}_3$ , respectively, (13) with most reducing agents, forms isopropyl alcohol  $(\text{CH}_3)_2\text{CHOH}$ , a secondary alcohol, but with sodium amalgam forms pinacone  $(\text{CH}_3)_2\text{COH} \cdot \text{COH}(\text{CH}_3)_2$  (14) with sodium dichromate and  $\text{H}_2\text{SO}_4$ , forms acetic acid  $\text{CH}_3\text{COOH}$  plus  $\text{CO}_2$ . When acetone vapor is passed through a tube at a dull red heat, ketene  $\text{CH}_2 : \text{CO}$  and methane  $\text{CH}_4$  are formed.

**ACETYL CHLORIDE.** See **Chlorinated Organics.**

**ACETYLENE.** [CAS: 74-86-2].  $\text{CH} : \text{CH}$  formula weight 26.04, mp  $-81.5^\circ\text{C}$ , bp  $-84^\circ\text{C}$ , 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  $\text{H}_2\text{O}$  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<sup>3</sup> (8.9 Cal/m<sup>3</sup>).

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<sub>2</sub>O 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<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub> or CHCl<sub>2</sub>·CHCl<sub>2</sub> or acetylene dichloride C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> or CHCl:CHCl, (2) with bromine, to form acetylene tetrabromide C<sub>2</sub>H<sub>2</sub>Br<sub>4</sub> or CHBr<sub>2</sub>·CHBr<sub>2</sub> or acetylene dibromide C<sub>2</sub>H<sub>2</sub>Br<sub>2</sub> or CHBr:CHBr, (3) with hydrogen chloride (bromide, iodide), to form ethylene monochloride CH<sub>2</sub>:CHCl (monobromide, monoiodide), and 1,1-dichloroethane, ethylene chloride CH<sub>2</sub>:CHCl<sub>2</sub> (dibromide, diiodide), (4) with H<sub>2</sub>O in the presence of a catalyzer, e.g., mercuric sulfate, to form acetaldehyde CH<sub>3</sub>·CHO, (5) with hydrogen, in the presence of a catalyzer, e.g., finely divided nickel heated, to form ethylene C<sub>2</sub>H<sub>4</sub> or ethane C<sub>2</sub>H<sub>6</sub>, (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<sub>2</sub>HNa and C<sub>2</sub>Na<sub>2</sub>. (7) With ammoniacuprous (or silver) salt solution, to form cuprous (or silver) acetylide C<sub>2</sub>Cu<sub>2</sub>, dark red precipitate, explosive when dry, and yielding acetylene upon treatment with acid, (8) with mercuric chloride solution, to form trichloromercuric acetaldehyde C(HgCl)<sub>3</sub>·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<sub>n</sub>H<sub>2n-2</sub>, 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<sub>6</sub>H<sub>4</sub>(COOH)CO<sub>2</sub>CH<sub>3</sub>, 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 hypogammaglobulinemia. 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. Histology-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  $\beta$ -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 ( $\text{SO}_2$ ) and oxides of nitrogen ( $\text{NO}_x$ ) 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  $\text{SO}_2$  emissions and 30 percent of  $\text{NO}_x$  emissions in the United States. Mobile sources (transportation) also contribute significantly to  $\text{NO}_x$  emissions. Overall, over 20 million tons of  $\text{SO}_2$  and  $\text{NO}_x$  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,  $\text{SO}_2$  and  $\text{NO}_x$  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  $\text{SO}_2$

and  $\text{NO}_x$ , 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  $\text{SO}_2$  and  $\text{NO}_x$  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  $\text{SO}_2$  emissions required by the Acid Rain Program will significantly reduce acidification due to atmospheric sulfur. Without the reductions in  $\text{SO}_2$  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



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