



# **McGraw-Hill Encyclopedia of CHEMISTRY**

**Sybil P. Parker**

**Editor in Chief**

**McGraw Hill Book Company**

New York St. Louis San Francisco

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1234567890 K P K P 89876543

ISBN 0-07-045484-1

#### **Library of Congress Cataloging in Publication Data**

McGraw-Hill encyclopedia of chemistry.

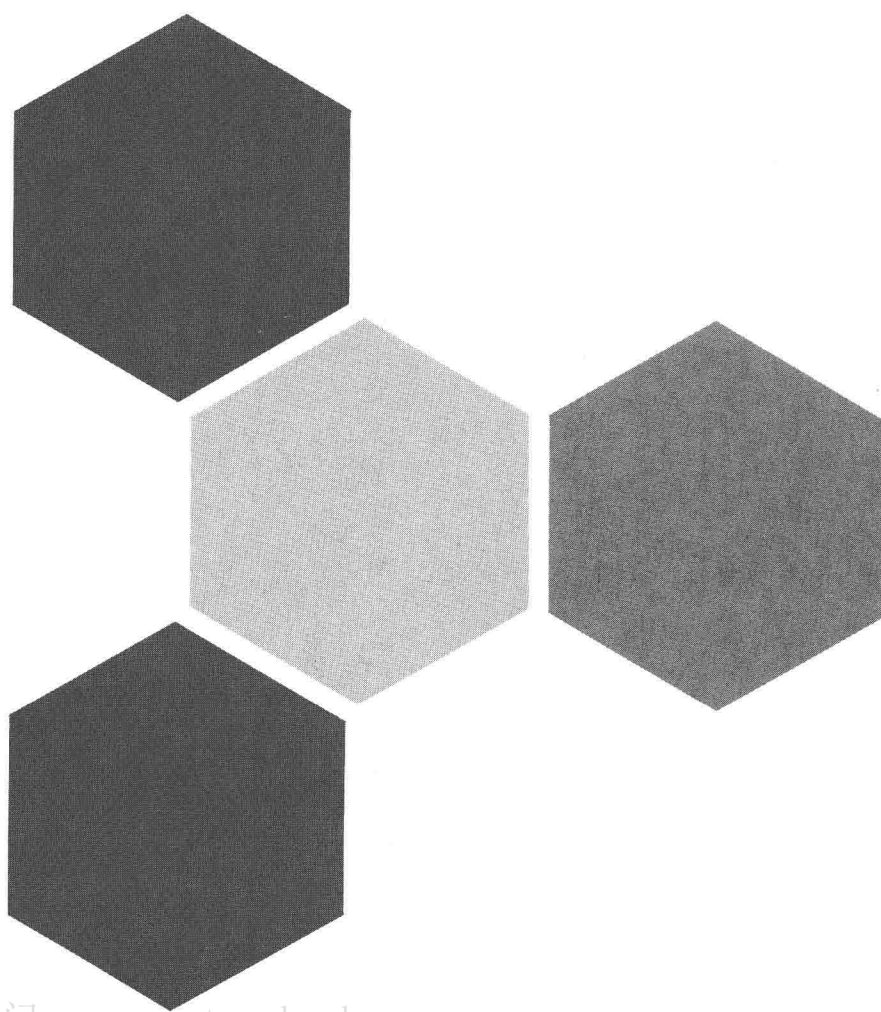
“All of the material in this volume has been published previously in the McGraw-Hill encyclopedia of science & technology, fifth edition” — T.p. verso.

Bibliography: p.

Includes index.

1. Chemistry — Dictionaries. I. Parker, Sybil P.  
II. McGraw-Hill Book Company. III. McGraw-Hill  
encyclopedia of science & technology. 5th ed.  
QD5.M36 1983 540'.3'21 82-21665  
ISBN 0-07-045484-1

**McGraw-Hill  
Encyclopedia of  
CHEMISTRY**



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## Preface

The science of chemistry is concerned with the composition and structure of matter—that is, its physical and chemical properties and its reactions. In this regard, chemistry is closely related to physics, especially in the study of the atom, since all matter is composed of elements whose properties are attributable to the nature of the atomic structure. This volume, therefore, not only covers the fundamental principles of chemistry but also includes relevant topics in physics that are essential for the understanding of modern chemistry.

The *Encyclopedia of Chemistry* is a comprehensive reference that will provide the reader with the most up-to-date information available on each of the major divisions of theoretical chemistry—inorganic, organic, physical, and analytical. In addition, articles explore the nature of matter from the perspective of atomic physics, quantum theory, statistical mechanics, and thermodynamics. Space limitations have precluded coverage of related fields of study such as biochemistry, geochemistry, agricultural chemistry, and chemical technology. The history of chemistry is discussed only if it applies to the development of subjects in individual articles.

This Encyclopedia is unique in both its scope and depth of coverage. Each article begins with a definition and presents a complete yet concise explanation of the subject in language as simple as the topic permits without omitting important technical information. The articles range from subjects as simple as nomenclature and the elements to sophisticated theoretical concepts such as molecular orbital theory. The Encyclopedia as a whole surveys the science of chemistry in nearly 800 articles, including Stereochemistry, Activation analysis, Heterogeneous catalysis, Polymer, Vacuum fusion, Acid-base indicator, Valence, Electron spin, and Organometallic compound.

The articles were selected from the *McGraw-Hill Encyclopedia of Science and Technology* (5th ed., 1982). The text is supplemented by hundreds of structural formulas, chemical reactions, graphs, tables, drawings, and photographs which clarify the presentation. All information is readily accessible through the detailed index and by the use of cross-references throughout. Bibliographies list publications that provide further information.

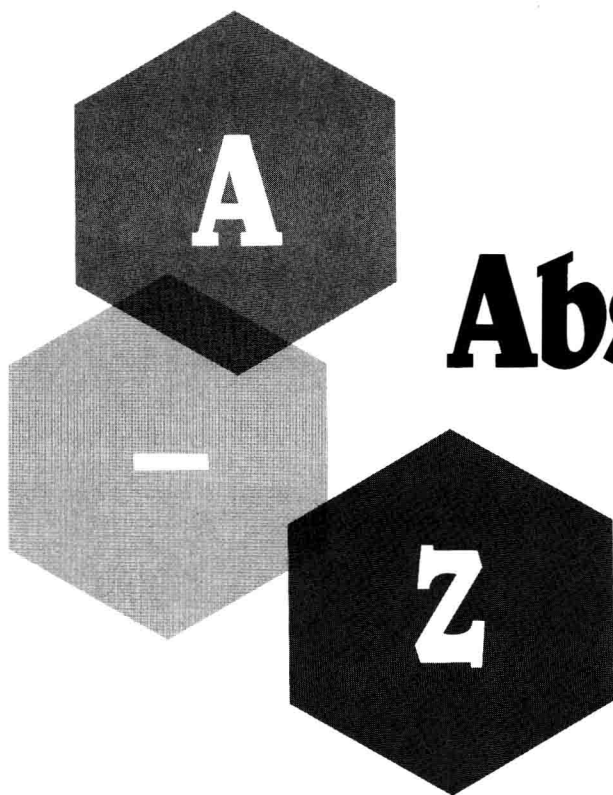
## viii Preface

We wish to thank the many Contributors whose work has been carried over to this specialized volume; and especially the Field Consultants, including Messrs. Bromley, Doscher, Good, Jarnagin, and Murray, whose expertise was invaluable in organizing the 1982 parent project. Two other Field Consultants, Messrs. Katz and Kopple, provided fresh impetus in developing the present volume, as unstinting Project Consultants.

This Encyclopedia is indispensable for chemists and other scientists, students, librarians, science writers, and anyone else needing basic information about chemistry in a readily accessible format.

**Sybil P. Parker**  
EDITOR IN CHIEF





# Absorption-Zirconium

## Absorption

Either the taking up of matter in bulk by other matter, as in the dissolving of a gas by a liquid; or the taking up of energy from radiation by the medium through which the radiation is passing. In the first case, an absorption coefficient is defined as the amount of gas dissolved at standard conditions by 1 cm<sup>3</sup> of the solvent. Absorption in this sense is a volume effect: The absorbed substance permeates the whole of the absorber. In absorption of the second type, attenuation is produced which in many cases follows Lambert's law and adds to the effects of scattering if the latter is present.

Absorption of electromagnetic radiation can occur in several ways. For example, microwaves in a wave guide lose energy to the walls of the guide: For nonperfect conductors, the wave penetrates the guide surface and energy in the wave is transferred to the atoms of the guide. Light is absorbed by atoms of the medium through which it passes, and in some cases, this absorption is quite distinctive: Selected frequencies from a heterochromatic source are strongly absorbed, as in the absorption spectrum of the Sun. Electromagnetic radiation can be absorbed by the photoelectric effect, where the light quantum is absorbed and an electron of the absorbing atom is ejected, and also by Compton scattering. Electron-positron pairs may be created by the absorption of a photon of sufficiently high energy. Photons can be absorbed by photoproduction of nuclear and subnuclear particles, analogous to the photoelectric effect.

Sound waves are absorbed at suitable frequencies by particles suspended in the air (wavelength

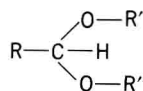
of the order of the particle size), where the sound energy is transformed into vibrational energy of the absorbing particles.

Absorption of energy from a beam of particles can occur by the ionization process, where an electron in the medium through which the beam passes is removed by the beam particles. The finite range of protons and  $\alpha$ -particles in matter is a result of this process. In the case of low-energy electrons, scattering is as important as ionization, so that range is a less well-defined concept. Particles themselves may be absorbed from a beam. For example, in a nuclear reaction an incident particle  $X$  is absorbed into nucleus  $Y$ , and the result may be that another particle  $Z$ , or a photon, or particle  $X$  with changed energy comes out. Low-energy positrons are quickly absorbed by annihilating with electrons in matter to yield two  $\gamma$ -rays.

[MC ALLISTER H. HULL, JR.]

## Acetals

Stable ethers usually prepared by acid-catalyzed alcoholation of the carbonyl group of aldehydes. The Y-shaped general formula for these compounds is shown below. (R represents an organic



radical.) Cyclic acetals (*meta*-dioxolanes, *meta*-dioxanes, and so forth) are formed from diols. Alcoholation of the carbonyl function of ketones yields analogous substances, ketals. Acetals may also be obtained through the Prins reaction of olefins with aldehydes, usually formaldehyde. The

acetals are stable toward alkalies, but they hydrolyze in the presence of acids. They are sometimes used to protect the aldehyde group during reactions and are useful substitutes for the simple ethers as solvents in synthetic chemistry, for example, in the Grignard reactions. Their thermal decomposition yields vinyl ethers. Few acetals have any large-scale industrial applications. Their hydrolytic stability to alkali commends the use of some in soaps as fragrances, and their solvency characteristics, in which they are similar to both esters and ethers, make them convenient solvents and plasticizers. Poly(formaldehyde) and certain copolymers of trioxane with epoxides or dioxolanes are called acetal resins because their main valence chains are sequences of acetal linkages. See ALDEHYDE; GLYCOL; KETONE.

[FRANK WAGNER]

*Bibliography:* D. Barton and W. D. Ollis (eds.), *Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds*, vol. 1, 1979.

## Acetate

One of two types of compounds derived from acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ . One type is obtained by the reaction of acetic acid and bases to give salts containing the negative acetate ion,  $\text{C}_2\text{H}_3\text{O}_2^-$ . The second type of compound is an ester which is derived from acetic acid and an alcohol, for example, ethyl acetate. Acetate is the official name (Federal Trade Commission) for the textile fiber produced from partially hydrolyzed cellulose acetate and once called acetate rayon.

All the metal acetates are water-soluble except silver acetate. The acetate ion is colorless; it may be identified by heating a sample with sulfuric acid to give the odor of acetic acid. The fruitlike odor of the ester formed when ethyl alcohol and a trace of sulfuric acid are heated with the sample is also characteristic. See ACETIC ACID; CARBOXYLIC ACID; ESTER.

[E. EUGENE WEAVER]

## Acetic acid

A colorless, pungent liquid,  $\text{CH}_3\text{COOH}$ , melting at  $16.7^\circ\text{C}$  and boiling at  $118.0^\circ\text{C}$ . Acetic acid is the sour principle in vinegar. Concentrated acid is called glacial acetic acid because of its readiness to crystallize at cool temperatures. Acetic acid in vinegar arises through an aerobic fermentation of dilute ethanol solutions, such as wine, cider, and beer, with any of several varieties of *Acetobacter*. Though there are several feasible ways to concentrate acetic acid from fermentation broths, none is currently considered economical.

**Production.** Acetic acid was formerly manufactured from pyroligneous acid obtained in destructive distillation of wood. These processes are of historical interest because many modern chemical engineering operations developed through the study of acetic acid production. Today acetic acid is manufactured by three main routes: butane liquid-phase catalytic oxidation in acetic acid solvent, palladium-copper salt-catalyzed oxidation of ethylene in aqueous solution, and methanol carbonylation in the presence of rhodium catalyst. Large quantities of acetic acid are recovered in the manufacture of cellulose acetate and polyvinyl

alcohol. Some acetic acid is produced in the oxidation of higher olefins, aromatic hydrocarbons, ketones, and alcohols. See OXIDATION PROCESS.

**Chemical properties.** Pure acetic acid is completely miscible with water, ethanol, diethyl ether, and carbon tetrachloride, but is not soluble in carbon disulfide. Freezing of acetic acid is accompanied by a remarkable volume contraction: the molar volume of liquid acetic acid at the freezing point is  $57.02\text{ cm}^3/\text{mole}$ , but at the same temperature the crystalline solid is  $47.44\text{ cm}^3/\text{mole}$ . It is a strongly proton-donating solvent with a relatively small dipole moment and a low dielectric constant. In a water solution, acetic acid is a typical weakly ionized acid ( $K_a = 1.8 \times 10^{-5}$ ). See CARBOXYLIC ACID.

The vapor density of acetic acid indicates a molecular weight considerably higher than would be expected for a compound with a formula weight of 60.05. The acid probably exists largely as the dimer in the vapor and liquid states.

Acetic acid neutralizes many oxides and hydroxides, and decomposes carbonates to furnish acetate salts, which are used in textile dyeing and finishing, as pigments, and as pesticides; examples are verdigris, white lead, and paris green. See ARSENIC; LEAD.

Over two-thirds of the acetic acid manufactured is used in production of either vinyl acetate or cellulose acetate. Acetic anhydride, the key intermediate in making cellulose acetate, is prepared commercially by pyrolysis of acetic acid in the presence of trialkyl phosphate catalyst. Considerable amounts of acetic acid are consumed in the manufacture of terephthalic acid by liquid-phase oxidation of xylene, and in the preparation of esters for lacquer solvents, paints and varnishes, pharmaceuticals, and herbicides. See ESTER; SOLVENT.

[FRANK WAGNER]

*Bibliography:* T. A. Geissman, *Principles of Organic Chemistry*, 4th ed., 1977; C. R. Noller, *Chemistry of Organic Compounds*, 3d ed., 1965; J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, 2d ed., 1977.

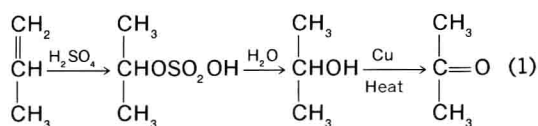
## Acetone

A chemical compound,  $\text{CH}_3\text{COCH}_3$ . A colorless liquid with an ethereal odor, it is the first member of the homologous series of aliphatic ketones. Its physical properties include boiling point  $56.2^\circ\text{C}$ , melting point  $-94.8^\circ\text{C}$ , and specific gravity 0.791. Acetone is an extremely important, low-cost raw material that is used for production of other chemicals.

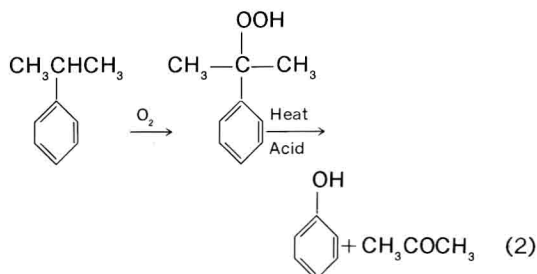
Acetone is used as a solvent for cellulose ethers, cellulose acetate, cellulose nitrate, and other cellulose esters. Cellulose acetate is spun from acetone solution. Lacquers, based on cellulose esters, are used in solution in mixed solvents including acetone. Acetylene is safely stored in cylinders under pressure by dissolving it in acetone, which is absorbed on inert material such as asbestos. It has a low toxicity.

**Production.** The principal method of acetone production uses propylene, obtained from the cracking of petroleum. Addition of sulfuric acid to propylene yields isopropyl hydrogen sulfate, which upon hydrolysis yields isopropyl alcohol. Oxidation or dehydrogenation over metal catalysts, such as

copper, converts the alcohol to acetone, as shown in reaction (1).

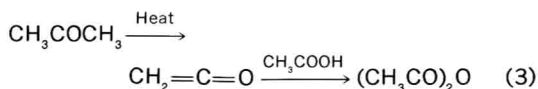


Acetone is also produced by passage of acetic acid vapor over metallic oxide catalysts at 400–450°C, by partial oxidation of the lower alkane hydrocarbons, and by the decomposition of cumene hydroperoxide, as shown in reaction (2).

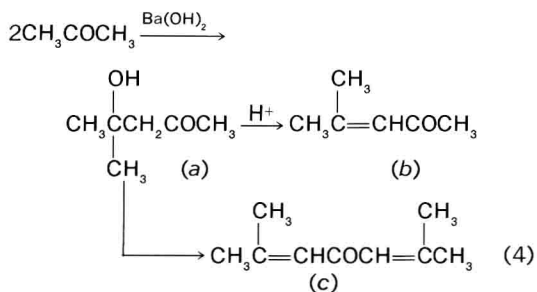


Phenol is the other product of this last process, which has been in operation in the United States since 1954.

**Chemical uses.** Pyrolysis of acetone vapor at 700°C produces ketene, which reacts with acetic acid to produce acetic anhydride, as shown in reaction (3).



Aldol-type condensation of acetone with  $\text{Ba}(\text{OH})_2$  yields (a) diacetone alcohol, (b) mesityl oxide, and (c) phorone, shown in reaction (4). Catalytic hydro-

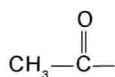


genation of mesityl oxide gives methyl isobutyl ketone. All these products are of commercial use as solvents or as chemical intermediates. See

[DAVID A. SHIRLEY]

## Acetylation

The introduction of an acetyl group



into an organic compound containing the alcoholic or phenolic hydroxyl ( $-\text{OH}$ ) or the amino ( $-\text{NH}_2$ ) and substituted amino groups to yield esters or substituted amides, respectively. The reaction can be used as a quantitative determination of the hy-

droxyl or amino group, and in qualitative organic analyses as a determination of the class of the amine. Acetylation can be carried out with acetic anhydride, acetyl chloride, or glacial acetic acid (in order of decreasing importance) and with or without an inert solvent, such as benzene or toluene. Often glacial acetic acid itself is used as a solvent and sulfuric acid is used as a catalyst. Ease of reaction is in the order of acetyl chloride > acetic anhydride > acetic acid. The first two often react at room temperature, whereas direct esterification with acetic acid usually requires more drastic conditions. Acetylation of acetylene is accomplished catalytically in the vapor phase or liquid phase to produce vinyl acetate. In general, acetylation reactions are exothermic.

The most important acetates formed by acetylation are cellulose acetate, vinyl acetate, and ethyl acetate. Cellulose acetate is prepared for use as a fiber (acetate rayon), safety movie film, and a tough plastic. Vinyl acetate is used in polymerization or copolymerization reactions to produce vinyl resins and cyclic acetals (safety glass). Ethyl acetate is one of many esters which are often prepared by a continuous process for use as a solvent.

Other important acetylation reactions include (1) production of pharmaceuticals such as aspirin, phenacetin, and derivatives; (2) protection of active groups during organic syntheses, particularly the amino and substituted amino group; (3) determination of the hydroxy acid content of fats and oils (acetyl number); (4) preparation of solid derivatives from liquids for qualitative identification; (5) differentiation of tertiary from primary and secondary amines; (6) preparation of  $\alpha, \beta$ -unsaturated acids and coumarin derivatives (Perkin reaction); (7) preparation of acid anhydrides with acetic anhydride and an organic acid by an exchange reaction; and (8) production of other chemical intermediates. See ACID ANHYDRIDE; ACID HALIDE; AMINE.

[ELBERT H. HADLEY]

*Bibliography:* S. H. Pine et al., *Organic Chemistry*, 4th ed., 1980.

## Acetylene

A colorless, aromatic gas that burns with a highly luminous flame, sublimates at  $-83.4^\circ\text{C}/760$  mmHg, and is shock-sensitive at low temperatures and partial pressures above 20–30 psia (138–207 kPa absolute). Acetylene is safely stored in cylinders under pressure, using acetone as a solvent. Acetylene burns with oxygen to produce the highest achievable flame temperature, over  $3300^\circ\text{C}$ , of any carbonaceous fuel. Oxyacetylene flames are of major importance in the welding and cutting of metals.

**Reactions.** Acetylene has the formula  $\text{HC}\equiv\text{CH}$ . The triple bond undergoes addition reactions to produce ethylene and ethane derivatives. Unsymmetrical reagents such as hydrogen chloride add to produce vinyl chloride and 1,1-dichloroethane; hydrogen cyanide produces acrylonitrile; acetic acid reacts to form vinyl acetate; and alcohols yield vinyl ethers. Water adds to acetylene in the presence of mercuric salts and strong acids to produce acetaldehyde, and chlorine adds to form 1,2-dichloroethene and 1,1,2,2-tetrachloroethane. The hydrogen atoms of acetylene undergo replacement reactions, demonstrating their moderate

## 4 Acetylide

acidity. Aqueous solutions of copper and silver salts produce explosive metal acetylides, for example,  $\text{AgC}\equiv\text{CAg}$ . Reactive metals, for example sodium, on contact with acetylene form stable mono- and disodium salts with the generation of hydrogen. Formaldehyde reacts to produce 1,4-butanediol, which can be hydrogenated to the commercially important 1,4-butanediol. Acetylene reacts with carbon monoxide and alcohols in the presence of nickel carbonyl to form acrylate esters.

**Production.** Acetylene was first produced commercially by contacting water and calcium carbide, a product of roasting calcium oxide with coke. In 1978 only about 5% of the world's production of 900,000 metric tons of acetylene was produced from calcium carbide. Modern processes generate acetylene by high-temperature hydrocarbon cracking reactions. Energy for the processes comes from externally generated steam, from internal partial oxidation of the feedstock, or by electric arc furnaces still in use in Europe. Raw materials range from methane through naphtha, and experimental processes have used crude oil and coal. About 15% of the acetylene produced in the United States is a by-product of ethylene manufacture from hydrocarbon gas cracking processes. The more favorable economics of ethylene production from hydrocarbons has caused acetylene to be replaced as a major raw material for many important commodity chemicals. As a consequence, since the mid-1960s world production of acetylene has been on the decline. By the late 1970s in the United States only 4% of the vinyl chloride and 10% of the vinyl acetate were manufactured from acetylene, ethylene being the preferred raw material.

The major growing use for acetylene is in the manufacture of 1,4-butanediol. This product is used as a chain extender for polyurethanes and in polybutylene terephthalate resins. Vinyl chloride, acrylic acid and esters, and vinyl acetate still constitute major uses for acetylene. See ALKYNE; THERMOCHEMISTRY.

[ROBERT K. BARNES]

*Bibliography:* S. A. Miller, *Acetylene*, 2 vols., 1965, 1966; C. A. Hampel and G. G. Hawley, *The Encyclopedia of Chemistry*, 3d ed., 1973.

### Acetylide

A derivative of acetylene formed by the replacement of one or both of the hydrogens by a metal. General formulas are  $\text{H}-\text{C}\equiv\text{C}-\text{M}$  and  $\text{M}-\text{C}\equiv\text{C}-\text{M}$ , the latter being known as carbides (although carbides such as  $\text{SiC}$ ,  $\text{B}_6\text{C}$ , and  $\text{WC}$  are not acetylides). Acetylides are prepared by the action of acetylene on active metals or metal compounds, or by the action of metals or metal compounds on carbon at high temperatures (electric furnace). Alkali and alkaline-earth acetylides are relatively stable, but most heavy metal derivatives are thermodynamically unstable and may explode when dry. They are readily decomposed by dilute acid. Acetylides are salts of a very weak acid and therefore hydrolyze readily. The most important acetylide is calcium carbide, which is used to prepare acetylene. Cuprous acetylide is used in ethynylation and high-pressure reactions. See ACETYLENE; CARBIDE.

[ELBERT H. HADLEY]

## Acid and base

Two interrelated classes of chemical compounds, the precise definitions of which have varied considerably with the development of chemistry. These changing definitions have led to frequent controversies, some of which are still unresolved. Acids initially were defined only by their common properties. They were substances which had a sour taste, which dissolved many metals, and which reacted with alkalis (or bases) to form salts. For a time, following the work of A. L. Lavoisier, it was believed that a common constituent of all acids was the element oxygen, but gradually it became clear that, if there were an essential element, it was hydrogen, not oxygen. In fact, the definition of an acid, formulated by J. von Liebig in 1840, as "a hydrogen-containing substance which will generate hydrogen gas on reaction with metals" proved to be satisfactory for about 50 years.

Bases initially were defined as those substances which reacted with acids to form salts (they were the "base" of the salt). The alkalis, soda and potash, were the best-known bases, but it soon became clear that there were other bases, notably ammonia and the amines.

Acids and bases are among the most important chemicals of commerce. The inorganic acids are often known as mineral acids, and among the most important are sulfuric,  $\text{H}_2\text{SO}_4$ ; phosphoric,  $\text{H}_3\text{PO}_4$ ; nitric,  $\text{HNO}_3$ ; and hydrochloric,  $\text{HCl}$  (sometimes called muriatic). Among the many important organic acids are acetic,  $\text{CH}_3\text{COOH}$ , and oxalic,  $\text{H}_2\text{C}_2\text{O}_4$ , acids, and phenol,  $\text{C}_6\text{H}_5\text{OH}$ . The important inorganic bases are ammonia,  $\text{NH}_3$ ; sodium hydroxide or soda,  $\text{NaOH}$ ; potassium hydroxide,  $\text{KOH}$ ; calcium hydroxide or lime,  $\text{Ca}(\text{OH})_2$ ; and sodium carbonate,  $\text{Na}_2\text{CO}_3$ . There are also many organic bases, mostly derivatives of ammonia. Examples are pyridine,  $\text{C}_5\text{H}_5\text{N}$ , and ethylamine,  $\text{C}_2\text{H}_5\text{NH}_2$ .

**Arrhenius-Ostwald theory.** When the concept of ionization of chemical compounds in water solution became established, some considerably different definitions of acids and bases became popular. Acids were defined as substances which ionized in aqueous solution to give hydrogen ions,  $\text{H}^+$ , and bases were substances which reacted to give hydroxide ions,  $\text{OH}^-$ . These definitions are sometimes known as the Arrhenius-Ostwald theory of acids and bases and were proposed separately by S. Arrhenius and W. Ostwald. Their use makes it possible to discuss acid and base equilibria and also the strengths of individual acids and bases. The ionization of an acid in water can be written as Eq. (1). Qualitatively, an acid is strong if



this reaction goes extensively toward the ionic products and weak if the ionization is only slight. A quantitative treatment of this ionization or dissociation can be given by utilizing the equilibrium expression for the acid, as shown in Eq. (2), where

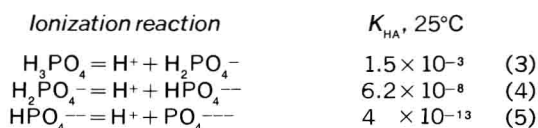
$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_{\text{HA}} \quad (2)$$

the brackets mean concentration in moles per liter and the constant  $K_{\text{HA}}$  is called the dissociation constant of the acid. This dissociation constant is a large number for a strong acid and a small number



for a weak acid. For example, at 25°C and with water as the solvent,  $K_{HA}$  has the value  $1.8 \times 10^{-5}$  for a typical weak acid, acetic acid (the acid of vinegar), and this value varies only slightly in dilute solutions as a function of concentration. Dissociation constants vary somewhat with temperature. They also change considerably with changes in the solvent, even to the extent that an acid which is fully ionized in water may, in some other less basic solvent, become decidedly weak. Almost all the available data on dissociation constants are for solutions in water, partly because of its ubiquitous character, and partly because it is both a good ionizing medium and a good solvent.

Acetic acid has only one ionizable hydrogen and is called monobasic. Some other acids have two or even three ionizable hydrogens and are called polybasic. An example is phosphoric acid, which ionizes in three steps, shown in Eqs. (3), (4), and (5), each with its own dissociation constant.



A similar discussion can be given for the ionization of bases in water. However, the concentrations of the species  $H^+$  and  $OH^-$  in a water solution are not independently variable. This is because water itself is both a weak acid and a weak base, ionizing very slightly according to Eq. (6). For pure



water, the concentrations of  $H^+$  and  $OH^-$  are equal. At ordinary temperatures, roughly  $2 \times 10^{-7}\%$  of the water is present as ions. As a result of this ionization, the ionic concentrations are related through Eq. (7). At 25°C and with concen-

$$\frac{[H^+][OH^-]}{[H_2O]} = K \quad (7)$$

trations in moles per liter, the product  $[H^+][OH^-]$  is equal to  $1 \times 10^{-14}$ .

A major consequence of this interdependence is that measurement of the concentration of either  $H^+$  or  $OH^-$  in a water solution permits immediate calculation of the other. This fact led S. P. L. Sørensen in 1909 to propose use of a logarithmic pH scale for the concentration of hydrogen ions in water. Although there are some difficulties in giving an exact definition of pH, it is very nearly correct for dilute solutions in water to write Eq. (8). It

$$pH = -\log [H^+] \quad (8)$$

then turns out that pH values of 0–14 cover the range from strongly acidic to strongly basic solutions. The pH of pure water at ordinary temperature is 7.

For many situations, it is desirable to maintain the  $H^+$  and  $OH^-$  concentration of a water solution at low and constant values. A useful device for this is a mixture of a weak acid and its anion (or of a weak base and its cation). Such a mixture is called a buffer. A typical example is a mixture of sodium acetate and acetic acid. From the treatment just given, it is evident that for this case Eq. (9)

$$[H^+] = \frac{[CH_3COOH]}{[CH_3COO^-]} \times 1.8 \times 10^{-5} \quad (9)$$

can be formed. In the equation  $[CH_3COOH]$  and  $[CH_3COO^-]$  represent the concentrations of acetic acid and acetate ion, respectively. Thus, if the concentrations of acetic acid and acetate ion are both 0.1 mole per liter, the  $H^+$  concentration will be  $1.8 \times 10^{-5}$  mole per liter and  $OH^-$  will be  $5.5 \times 10^{-10}$  mole per liter. The pH of this solution will be about 4.7. Constant acidity is a most important aspect of blood and other life fluids; these invariably contain weak acids and bases to give the necessary buffering action.

**Brönsted theory.** The Arrhenius, or water, theory of acid and bases has many attractive features, but it has also presented some difficulties. A major difficulty was that solvents other than water can be used for acids and bases and thus need consideration. For many of the solvents of interest, the necessary extensions of the water theory are both obvious and plausible. For example, with liquid ammonia as the solvent, one can define  $NH_4^+$  as the acid ion and  $NH_2^-$  as the base ion, and the former can be thought of as a hydrogen ion combined with a molecule of the solvent. However, for a hydrogenless (aprotic) solvent, such as liquid sulfur dioxide, the extensions are less obvious. Consideration of such systems has led to some solvent-oriented theories of acids and bases to which the names of E. C. Franklin and A. F. D. Germann often are attached. The essence of these theories is to define acids and bases in terms of what they do to the solvent. Thus, one definition of an acid is that it gives rise to "a cation which is characteristic of the solvent," for example,  $SO^{++}$  from sulfur dioxide. These theories have been useful in emphasizing the need to consider nonaqueous systems. However, they have not been widely adopted, at least partly because a powerful and wide-ranging protonic theory of acids and bases was introduced by J. N. Brönsted in 1923 and was rapidly accepted by many other scientists. Somewhat similar ideas were advanced almost simultaneously by T. M. Lowry, and the new theory is occasionally called the Brönsted-Lowry theory.

This theory gives a unique role to the hydrogen ion, and there appeared to be justification for this. One justification, of course, was the historically important role already given to hydrogen in defining acids. A rather different justification involved the unique structure of hydrogen ion. It is the only common ion which consists solely of a nucleus, the proton. As a consequence, it is only about  $10^{-14}$  cm in diameter. All other ordinary ions have peripheral electron clouds and, as a result, are roughly  $10^6$  times larger than the proton. The small size of the latter makes it reasonable to postulate that protons are never found in a free state but rather always exist in combination with some base. The Brönsted theory emphasizes this by proposing that all acid-base reactions consist simply of the transfer of a proton from one base to another.

The Brönsted definitions of acids and bases are: An acid is a species which can act as a source of protons; a base is a species which can accept protons. Compared to the water theory, this represents only a slight change in the definition of an acid but a considerable extension of the term base. In addition to hydroxide ion, the bases now include a wide variety of uncharged species, such as ammonia and the amines, as well as numerous

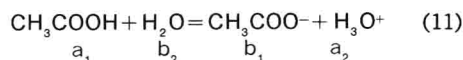
Conjugate acid-base pairs

	Acids		Bases	
Strong acids	H <sub>2</sub> SO <sub>4</sub>	—————	HSO <sub>4</sub> <sup>-</sup>	Weak bases
	HCl	—————	Cl <sup>-</sup>	
	H <sub>3</sub> O <sup>+</sup>	—————	H <sub>2</sub> O	
	HSO <sub>4</sub> <sup>-</sup>	—————	SO <sub>4</sub> <sup>2-</sup>	
	HF	—————	F <sup>-</sup>	
	CH <sub>3</sub> <sup>(aq)</sup> COOH	—————	CH <sub>3</sub> COO <sup>-</sup>	
	NH <sub>4</sub> <sup>+</sup>	—————	NH <sub>3</sub>	
	HCO <sub>3</sub> <sup>-</sup>	—————	CO <sub>3</sub> <sup>2-</sup>	
Weak acids	H <sub>2</sub> O	—————	OH <sup>-</sup>	Strong bases
	C <sub>2</sub> H <sub>5</sub> OH	—————	C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>	

charged species, such as the anions of weak acids. In fact, every acid can generate a base by loss of a proton. Acids and bases which are related in this way are known as conjugate acid-base pairs, and the table lists several examples. By these definitions, such previously distinct chemical processes as ionization, hydrolysis, and neutralization become examples of the single class of proton transfer or protolytic reactions. The general reaction is expressed as Eq. (10). This equation can be



considered to be a combination of two conjugate acid-base pairs, and the pairs below can be used to construct a variety of typical acid-base reactions. For example, the ionization of acetic acid in water becomes Eq. (11). Water functions here as a base



to form the species H<sub>3</sub>O<sup>+</sup>, the oxonium ion (sometimes called the hydronium ion). However, water can also function as an acid to form the base OH<sup>-</sup>, and this dual or amphoteric character of water is one reason why so many acid-base reactions occur in it.

As the table shows, strengths of acids and bases are not independent. A very strong Brönsted acid implies a very weak conjugate base and vice versa. A qualitative ordering of acid strength or base strength, as above, permits a rough prediction of the extent to which an acid-base reaction will go. The rule is that a strong acid and a strong base will react extensively with each other, whereas a weak acid and a weak base will react together only very slightly. More accurate calculations of acid-base equilibria can be made by using the ordinary formulation of the law of mass action. A point of some importance is that, for ionization in water, the equations reduce to the earlier Arrhenius-Ostwald type. Thus, for the ionization of acetic acid in water Eq. (11) leads to Eq. (12). Remembering that

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]} = K \quad (12)$$

the concentration of water will be almost constant since it is the solvent, this can be written as Eq. (13), where  $K_{\text{HAc}}$  is just the conventional dissociation constant for acetic acid in water.

$$\frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = K[\text{H}_2\text{O}] \equiv K_{\text{HAc}} \quad (13)$$

One result of the Brönsted definitions is that for a given solvent, such as water, there is only a sin-

gle scale of acid-base strength. Put another way, the relative strength of a set of acids will be the same for any base. Hence, the ordinary tabulation of ionization constants of acids in water permits quantitative calculation for a very large number of acid-base equilibria.

The Brönsted concepts can be applied without difficulty to other solvents which are amphoteric in the same sense as water, and data are available for many nonaqueous solvents, such as methyl alcohol, formic acid, and liquid ammonia. An important practical point is that relative acid (or base) strength turns out to be very nearly the same in these other solvents as it is in water. Brönsted acid-base reactions can also be studied in aprotic solvents (materials such as hexane or carbon tetrachloride which have virtually no tendency to gain or lose protons), but in this case, both the acid and the base must be added to the solvent.

A fact which merits consideration in any theory of acids and bases is that the speeds of large numbers of chemical reactions are greatly accelerated by acids and bases. This phenomenon is called acid-base catalysis, and a major reason for its wide prevalence is that most proton transfers are themselves exceedingly fast. Hence, reversible acid-base equilibria can usually be established very rapidly, and the resulting conjugate acids (or bases) then frequently offer favorable paths for the overall chemical reaction. The mechanisms of many of these catalyzed reactions are known. Some of them are specifically catalyzed by solvated protons (hydrogen ions); others, by hydroxide ions. Still others are catalyzed by acids or bases in the most general sense of the Brönsted definitions. The existence of this general acid and base catalysis constituted an important item in the wide acceptance of the Brönsted definitions.

**Lewis theory.** Studies of catalysis have, however, played a large role in the acceptance of a set of quite different definitions of acids and bases, those due to G. N. Lewis. These definitions were originally proposed at about the same time as those of Brönsted, but it was not until Lewis restated them in 1938 that they began to gain wide consideration. The Lewis definitions are: An acid is a substance which can accept an electron pair from a base; a base is a substance which can donate an electron pair. (These definitions are very similar to the terms popularized around 1927 by N. V. Sidgwick and others: electron donors, which are essentially Lewis bases, and electron acceptors, which are Lewis acids.) Bases under the Lewis definition are very similar to those defined by Brönsted, but the Lewis definition for acids is very much broader. For example, virtually every cation is an acid, as are such species as AlCl<sub>3</sub>, BF<sub>3</sub>, and SO<sub>3</sub>. An acid-base reaction now typically becomes a combination of an acid with a base, rather than a proton transfer. Even so, many of the types of reactions which are characteristic of proton acids also will occur between Lewis acids and bases, for example, neutralization and color change of indicators as well as acid-base catalysis. Furthermore, these new definitions have been useful in suggesting new interrelations and in predicting new reactions, particularly for solid systems and for systems in nonaqueous solvents.

For several reasons, these definitions have not

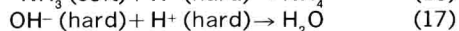
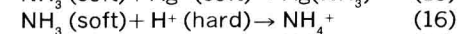
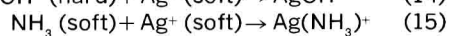
been universally accepted. One reason is that the terms electron donor and electron acceptor had been widely accepted and appear to serve similar predicting and classifying purposes. A more important reason is unwillingness to surrender certain advantages in precision and definiteness inherent in the narrower Brönsted definitions. It is a drawback of the Lewis definitions that the relative strengths of Lewis acids vary widely with choice of base and vice versa. For example, with the Brönsted definitions, hydroxide ion is always a stronger base than ammonia; with the Lewis definitions, hydroxide ion is a much weaker base than ammonia when reacting with silver ion but is stronger than ammonia when reacting with hydrogen ion. Another feature of the Lewis definitions is that some substances which have long been obvious examples of acids, for example, HCl and  $\text{H}_2\text{SO}_4$ , do not naturally fit the Lewis definition since they cannot plausibly accept electron pairs. Certain other substances, for example, carbon dioxide, are included by calling them secondary acids. These substances, too, tend to have electronic structures in which the ability to accept electron pairs is not obvious, but the more important distinction between them and primary acids is that their rates of neutralization by bases are measurably slow. However, in spite of these difficulties, the use of the Lewis definitions is increasing. Since there does not appear to be any simultaneous tendency to abandon the Brönsted definitions, chemistry seems to be entering a period when the term acid needs a qualifying adjective for clarity, for example, Lewis acid or proton acid.

**Hard and soft acids and bases.** As pointed out above, one of the drawbacks of such a broad definition as the Lewis one is that it is difficult to systematize the behavior of acids and bases toward each other. Attempts have been made to classify Lewis acids and bases into categories with respect to their mutual behavior. R. G. Pearson in 1963 proposed a simple and lucid classification scheme, based in part on earlier methods, that appears to be promising in its application to a wide variety of Lewis acid-base behavior.

Lewis bases (electron donors) are classified as soft if they have high polarizability, low electronegativity, are easily oxidized, or possess low-lying empty orbitals. They are classified as hard if they have the opposite tendencies. Some bases, spanning the range of hard to soft and listed in order of increasing softness, are  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{OCH}_3^-$ ,  $\text{F}^-$ ,  $\text{NH}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ ,  $\text{NO}_2^-$ ,  $\text{NH}_2\text{OH}$ ,  $\text{N}_3\text{H}_4$ ,  $\text{C}_6\text{H}_5\text{SH}$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $(\text{C}_6\text{H}_5)_3\text{P}$ . Acids are divided more or less distinctly into two categories, hard and soft, with a few intermediate cases. Hard acids are of low polarizability, small size, and high positive oxidation state, and do not have easily excitable outer electrons. Soft acids have several of the properties of high polarizability, low or zero positive charge, large size, and easily excited outer electrons, particularly *d* electrons in metals. Some hard acids are  $\text{H}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Be}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$ ,  $\text{Mn}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Sc}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Co}^{+3}$ ,  $\text{Fe}^{+3}$ ,  $\text{As}^{+3}$ ,  $\text{Ce}^{+3}$ ,  $\text{Si}^{+4}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$ ,  $\text{Pu}^{+4}$ ,  $\text{BeMe}_2$  (Me is the methyl group),  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{B(OR)}_3$ ,  $\text{Al(CH}_3)_3$ ,  $\text{AlH}_3$ ,  $\text{SO}_3$ , and  $\text{CO}_2$ . Examples of soft acids are  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{Tl}^+$ ,  $\text{Hg}^+$ ,  $\text{Cs}^+$ ,  $\text{Pd}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Pt}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{CH}_3\text{Hg}^+$ ,  $\text{Ti}^{+3}$ ,  $\text{BH}_3$ ,  $\text{CO(CN)}_5^{2-}$ ,  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{ICN}$ ,

chloranil, quinones, tetracyanoethylene, O, Cl, Br, I, N, metal atoms, and bulk metals. Intermediate acids are  $\text{Fe}^{+2}$ ,  $\text{Co}^{+2}$ ,  $\text{Ni}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Sn}^{+2}$ ,  $\text{B(CH}_3)_3$ ,  $\text{SO}_2$ ,  $\text{NO}^+$ , and  $\text{R}_3\text{C}^+$ .

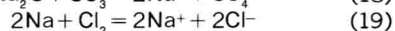
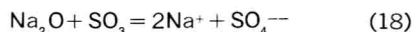
The rule for correlating acid-base behavior is then stated as: Hard acids prefer to associate with hard bases and soft acids with soft bases. Application, for example, to the problem of  $\text{OH}^-$  and  $\text{NH}_3$ , mentioned earlier (and recognizing that  $\text{OH}^-$  is hard compared with  $\text{NH}_3$ ), leads to Eq. (14), which is unfavorable compared with Eq. (15). However, the reaction shown in Eq. (16) is unfavorable compared with the reaction shown in Eq. (17), which is in agreement with experiment.



The rule is successful in correlating general acid-base behavior of a very wide variety of chemical systems, including metal-ligand interaction, charge-transfer complex formation, hydrogen bond formation, complex ion formation, carbonium ion formation, covalent bond formation, and ionic bond formation.

It is to be emphasized that the hard-and-soft acid-and-base concept is a means of classification and correlation and is not a theoretical explanation for acid-base behavior. The reasons why hard acids prefer hard bases and soft prefer soft are complex and varied. The already well-developed concepts of ionic and covalent bonds appear to be helpful, however. Hard acids and hard bases with small sizes and high charge would be held together with stable ionic bonds. Conversely, the conditions for soft acids and soft bases would be favorable for good covalent bonding. Existing theories of  $\pi$ -bonding also fit into the scheme.

**Usanovich theory.** Another comprehensive theory of acids and bases was proposed by M. Usanovich in 1939 and is sometimes known as the positive-negative theory. Acids are defined as substances which form salts with bases, give up cations, and add themselves to anions and to free electrons. Bases are similarly defined as substances which give up anions or electrons and add themselves to cations. Two examples of acid-base reactions under this scheme are Eqs. (18) and (19).



In the first,  $\text{SO}_3$  is an acid because it takes up an anion,  $\text{O}^{--}$ , to form  $\text{SO}_4^{--}$ . In the second example,  $\text{Cl}_2$  is an acid because it takes up electrons to form  $\text{Cl}^-$ . Using conventional terminology, this second reaction is an obvious example of oxidation-reduction. The fact that oxidation-reduction can also be included in the Usanovich scheme is an illustration of the extensiveness of these definitions. So far, this theory has had little acceptance, quite possibly because the definitions are too broad to be very useful.

**Generation of chemical species.** The acidic or basic character of a solvent can be used to stabilize interesting chemical species, which would otherwise be difficult to obtain. For example, carbonium ions have been thought to be important



intermediates in many organic reactions, but because of their fleeting existence as intermediates, their properties have been difficult to study. Most carbonium ions are very strong bases and would, for example, react, as shown by reaction (20). Ac-



cordingly, the equilibrium would lie far to the right. However, use of a very strongly acidic solvent reverses the reaction, and measurable amounts of carbonium ion are then found. Concentrated sulfuric acid has found use in this connection. The very high acidity of  $SbF_5$  by itself, as a Lewis acid, and in mixtures with other Lewis acids, such as  $SO_2$ , or protonic acids, such as HF and  $FSO_3H$ , makes possible the study of many otherwise unstable carbonium ions. See SUPERACIDS.

**Acidity functions.** A very different approach to the definition of acids, or perhaps better, to the definition of acidity, is to base the definition on a particular method of measurement. (As one example, it is probably true that the most nearly exact definition of pH is in terms of the electromotive force of a particular kind of galvanic cell.) It is possible to define various acidity functions in this way, and several have been proposed. One of the earliest and also one of the most successful is the  $H_0$  acidity function of L. P. Hammett. This defines an acidity in terms of the observed indicator ratio for a particular class of indicators, those which are uncharged in the basic form B. Suppose there is available a set of such indicators, and suppose further that the values of the dissociation constants of the acid forms  $BH^+$  are known. Then the  $h_0$  acidity of a solution is defined as Eq. (21), where  $K_{BH^+}$  is

$$h_0 = K_{BH^+} \frac{[BH^+]}{[B]} \quad (21)$$

the dissociation constant for the particular indicator employed, and where  $[BH^+]/[B]$  is the experimentally observed ratio of concentrations of the conjugate acid and conjugate base forms of the indicator. To have a logarithmic scale (analogous to pH), the further definition is expressed in Eq. (22). The virtues of this scale are that measure-

$$H_0 = -\log h_0 \quad (22)$$

ments are relatively simple and can be made for concentrated solutions and for solutions in non-aqueous or mixed solvents, situations where the pH scale offers difficulties. A further point is that in dilute aqueous solutions this new acidity becomes identical to pH. Although it has been found that this measure of acidity is fairly consistent within a class of indicators used, different classes can give somewhat different measures of acidity. Hence, caution must be used in interpretation of acidity measured by this technique.

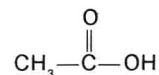
For a discussion of measurement of acidity see HYDROGEN ION. See also BASE; BUFFERS; IONIC EQUILIBRIUM; OXIDATION-REDUCTION; SOLUTION; SOLVENT.

[FRANKLIN A. LONG; RICHARD H. BOYD]

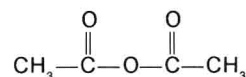
**Bibliography:** J. F. Coetzee and C. D. Ritchie, *Solute-Solvent Interactions*, 1969; J. J. Lagowski, *The Chemistry of Non-Aqueous Solvents*, vol. 1-3, 1966-1970, vol. 4, 1976; G. Olah, *Chem. Eng. News*, 45:77, Mar. 27, 1967; R. G. Pearson, Acids and bases, *Science*, 151:172, 1966.

## Acid anhydride

One of an important class of reactive organic compounds derived from acids via formal intermolecular dehydration; thus, acetic acid,

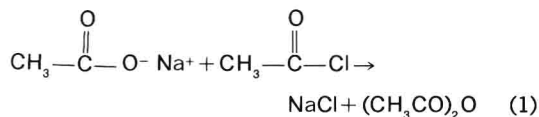


on loss of water forms acetic anhydride,

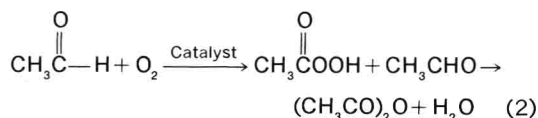


Anhydrides of straight-chain acids containing from 2 to 12 carbon atoms are liquids with boiling points higher than those of the parent acids. They are relatively insoluble in cold water and are soluble in alcohol, ether, and other common organic solvents. The lower members are pungent, corrosive, and weakly lacrimatory. Anhydrides from acids with more than 12 carbon atoms and cyclic anhydrides from dicarboxylic acids are crystalline solids.

**Preparation.** Because the direct intermolecular removal of water from organic acids is not practicable, anhydrides must be prepared by means of indirect processes. A general method involves interaction of an acid salt with an acid chloride, reaction (1).

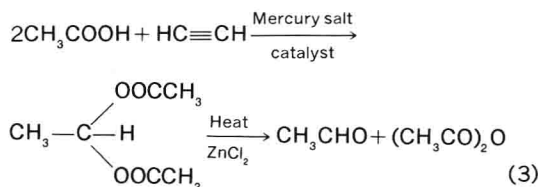


Acetic anhydride, the most important aliphatic anhydride, is manufactured by air oxidation of acetaldehyde, using as catalysts the acetates of copper and cobalt, shown in reaction (2); peracetic

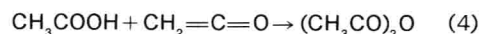


acid apparently is an intermediate. The anhydride is separated from the by-product water by vacuum distillation.

Another important process utilizes the thermal decomposition of ethylidene acetate (made from acetylene and acetic acid), reaction (3).

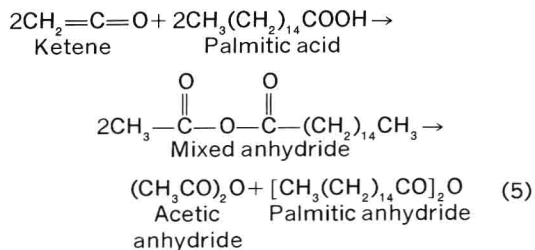


Acetic anhydride has been made by the reaction of acetic acid with ketene, reaction (4).



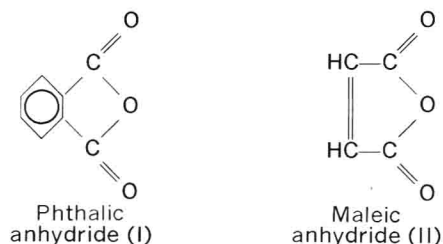
Mixed anhydrides composed of two different radicals are unstable, and disproportionate to give the two simple anhydrides. Direct use is made of this in the preparation of high-molecular-weight

anhydrides, as seen in reaction (5). The two simple



anhydrides are easily separable by distillation in a vacuum.

Cyclic anhydrides are obtained by warming succinic or glutaric acids, either alone, with acetic anhydride, or with acetyl chloride. Under these conditions, adipic acid first forms linear, polymeric anhydride mixtures, from which the monomer is obtained by slow, high-vacuum distillation. Cyclic anhydrides are also formed by simple heat treatment of cis-unsaturated dicarboxylic acids, for example, maleic and glutaric acids; and of aromatic 1,2-dicarboxylic acids, for example, phthalic acid. Commercially, however, both phthalic (I) and maleic (II) anhydrides are primary products of manufacture, being formed by vapor-phase, catalytic (vanadium pentoxide), air oxidation of naphthalene and benzene, respectively; at the reaction temperature, the anhydrides form directly.



**Uses.** Large quantities of anhydrides are used in the preparation of esters. Ethyl acetate and butyl acetate (from butyl alcohol and acetic anhydride) are excellent solvents for cellulose nitrate lacquers. Acetates of high-molecular-weight alcohols are used as plasticizers for plastics and resins. Cellulose and acetic anhydride give cellulose acetate, used in acetate rayon and photographic film. The reaction of anhydrides with sodium peroxide forms peroxides (acetyl peroxide is violently explosive), used as catalysts for polymerization reactions and for addition of alkyl halides to alkenes. In Friedel-Crafts reactions, anhydrides react with aromatic compounds, forming ketones such as acetophenone.

Maleic anhydride reacts with many dienes to give hydroaromatics of various complexities (Diels-Alder reaction). Much maleic anhydride is used commercially in the manufacture of alkyd resins from polyhydric alcohols. Soil conditioners are produced by basic hydrolysis of the copolymer of maleic anhydride with vinyl acetate.

Phthalic anhydride and alcohols form esters (phthalates) used as plasticizers for plastics and resins. Condensed with phenols and sulfuric acid, phthalic anhydride yields phthaleins, such as phenolphthalein; with *m*-dihydroxybenzenes under the same conditions, xanthene dyes form, for example, fluorescein. Much phthalic anhydride is

used in manufacturing glyptal resins (from the anhydride and glycerol) and in manufacturing anthraquinone. Heating phthalic anhydride with ammonia gives phthalimide, used in Gabriel's synthesis of primary amines, amino acids, and anthranilic acid (*o*-aminobenzoic acid). With alkaline hydrogen peroxide, phthalic anhydride yields monoperoxyphthalic acid, used along with benzoyl peroxide as polymerization catalysts, and as bleaching agents for oils, fats, and other edibles.

Anhydrides react with water to form the parent acid, with alcohols to give esters, and with ammonia to yield amides; and with primary or secondary amines, they furnish *N*-substituted and *N,N*-disubstituted amides, respectively. See ACID HALIDE; ACYLATION; CARBOXYLIC ACID; DIELS-ALDER REACTION; ESTER; FRIEDEL-CRAFTS REACTION.

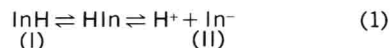
[PAUL E. FANTA]

*Bibliography:* N. L. Allinger et al., *Organic Chemistry*, 2d ed., 1976.

## Acid-base indicator

A substance that reveals, through characteristic color changes, the degree of acidity or basicity of solutions. Indicators are weak organic acids or bases which exist in more than one structural form (tautomers) of which at least one form is colored. Intense color is desirable so that very little indicator is needed; the indicator itself will thus not affect the acidity of the solution.

The equilibrium reaction of an indicator may be regarded typically by giving it the formula  $\text{HIn}$ . It dissociates into  $\text{H}^+$  and  $\text{In}^-$  ions and is in equilibrium with a tautomer  $\text{InH}$  which is either a non-electrolyte or at most ionizes very slightly. In the overall equilibrium shown as Eq. (1) the simplify-



ing assumption that the indicator exists only in forms (I) and (II) leads to no difficulty. The addition of acid will completely convert the indicator to form (I), which is therefore called the acidic form of the indicator although it is functioning as a base. A hydroxide base converts the indicator to form (II) with the formation of water; this is called the alkaline form. For the equilibrium between (I) and (II) the equilibrium constant is given by Eq. (2). In

$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{InH}]} \quad (2)$$

a manner similar to the pH designation of acidity, that is,  $\text{pH} = -\log[\text{H}^+]$ , the  $K_{\text{In}}$  is converted to  $\text{p}K_{\text{In}}$  with the result shown in Eq. (3). It is seen that the

$$\text{p}K_{\text{In}} = \text{pH} - \log \frac{[\text{In}^-]}{[\text{InH}]} \quad (3)$$

pK of an indicator has a numerical value approximately equal to that of a specific pH level.

**Use of indicators.** Acid-base indicators are commonly employed to mark the end point of an acid-base titration or to measure the existing pH of a solution. For titration the indicator must be so chosen that its pK is approximately equal to the pH of the system at its equivalence point. For pH