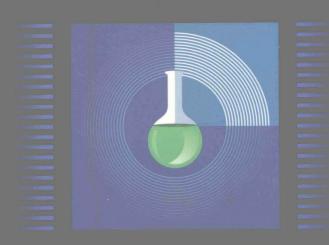
# McGRAW-HILL CONCISE ENCYCLOPEDIA of CHEMISTRY

- Over 700 condensed, illustrated articles on chemistry basics
  - Explanations, not definitions
- Every major chemistry area included



# CONCISE ENCYCLOPEDIA OF CHEMISTRY

### McGraw-Hill

### The McGraw·Hill Companies

### Library of Congress Cataloging in Publication Data

McGraw-Hill concise encyclopedia of chemistry.

p. cm.

Includes index

ISBN 0-07-143953-6

1. Chemistry—Encyclopedias. I. Title: Concise encyclopedia of chemistry.

QD4.M34 2004 540.3—dc22

2004049906

This material was extracted from the McGraw-Hill Encyclopedia of Science & Technology, Ninth Edition, © 2002 by The McGraw-Hill Companies, Inc. All rights reserved.

McGRAW-HILL CONCISE ENCYCLOPEDIA OF CHEMISTRY, copyright © 2004 by The McGraw-Hill Companies, Inc. All rights reserved. Printed in the United States of America. Except as permitted under the United States Copyright Act of 1976, no part of this publication may be reproduced or distributed in any form or by any means, or stored in a database or retrieval system, without the prior written permission of the publisher.

234567890 DOC/DOC 098765

This book was printed on acid-free paper.

It was set in Helvetica Black and Souvenir by TechBooks, Fairfax, Virginia.

The book was printed and bound by RR Donnelley, The Lakeside Press.

### **EDITORIAL STAFF**

Mark D. Licker, Publisher

Elizabeth Geller, Managing Editor
Jonathan Weil, Senior Staff Editor
David Blumel, Editor
Alyssa Rappaport, Editor
Charles Wagner, Manager, Digital Content
Renee Taylor, Editorial Assistant

# EDITING, DESIGN, AND PRODUCTION STAFF

Roger Kasunic, Vice President—Editing, Design, and Production

Joe Faulk, Editing Manager
Frank Kotowski, Jr., Senior Editing Supervisor
Ron Lane, Art Director
Vincent Piazza, Assistant Art Director
Thomas G. Kowalczyk, Production Manager
Pamela A. Pelton, Senior Production Supervisor

### CONSULTING EDITORS

- Dr. Milton B. Adesnik. Department of Cell Biology, New York University School of Medicine, New York. CELL BIOLOGY.
- Barry A. J. Fisher. Director, Scientific Services Bureau, Los Angeles County Sheriff's Department, Los Angeles, California. FORENSIC SCIENCE AND TECHNOLOGY.
- **Dr. Cynthia Larive.** Department of Chemistry, University of Kansas, Lawrence. INORGANIC CHEMISTRY.
- Prof. Chao-Jun Li. Canada Research
  Chair in Green Chemistry, Department of
  Chemistry, McGill University, Montreal,
  Quebec, Canada. ORGANIC CHEMISTRY.
- **Prof. Krzysztof Matyjaszewski.** J. C. Warner Professor of Natural Sciences,

- Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania. POLYMER SCIENCE AND ENGINEERING.
- Prof. Arthur A. Spector. Department of Biochemistry, University of Iowa, Iowa City. BIOCHEMISTRY.
- Prof. Mary Anne White. Killam Research Professor in Materials Science, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada. MATERIALS SCIENCE AND METALLURGIC ENGINEERING.
- Dr. Gary Wnek. Department of Chemical Engineering, Virginia Commonwealth University, Richmond. CHEMICAL ENGINEERING.

### **PREFACE**

For more than four decades, the *McGraw-Hill Encyclopedia of Science & Technology* has been an indispensable scientific reference work for a broad range of readers, from students to professionals and interested general readers. Found in many thousands of libraries around the world, its 20 volumes authoritatively cover every major field of science. However, the needs of many readers will also be served by a concise work covering a specific scientific or technical discipline in a handy, portable format. For this reason, the editors of the *Encyclopedia* have produced this series of paperback editions, each devoted to a major field of science or engineering.

The articles in this McGraw-Hill Concise Encyclopedia of Chemistry cover all the principal topics of this field. Each one is a condensed version of the parent article that retains its authoritativeness and clarity of presentation, providing the reader with essential knowledge in chemistry without extensive detail. The authors are international experts, including Nobel Prize winners. The initials of the authors are at the end of the articles; their full names and affiliations are listed in the back of the book.

The reader will find over 700 alphabetically arranged entries, many illustrated with diagrams or images. Most include cross references to other articles for background reading or further study. Dual measurement units (U.S. Customary and International System) are used throughout. The Appendix includes useful information complementing the articles. Finally, the Index provides quick access to specific information in the articles.

This concise reference will fill the need for accurate, current scientific and technical information in a convenient, economical format. It can serve as the starting point for research by anyone seriously interested in science, even professionals seeking information outside their own specialty. It should prove to be a much used and trusted addition to the reader's bookshelf.

MARK D. LICKER
Publisher

## ORGANIZATION OF THE FNCYCLOPEDIA

**Alphabetization.** The more than 700 article titles are sequenced on a word-byword basis, not letter by letter. Hyphenated words are treated as separate words. In occasional inverted article titles, the comma provides a full stop. The index is alphabetized on the same principles. Readers can turn directly to the pages for much of their research. Examples of sequencing are:

Acid and base
Acid anhydride
Acid-base indicator
Acid halide

Alkali metals Alkaline-earth metals Alkylation (petroleum)

**Cross references.** Virtually every article has cross references set in CAPITALS AND SMALL CAPITALS. These references offer the user the option of turning to other articles in the volume for related information.

**Measurement units.** Since some readers prefer the U.S. Customary System while others require the International System of Units (SI), measurements in the Encyclopedia are given in dual units.

**Contributors.** The authorship of each article is specified at its conclusion, in the form of the contributor's initials for brevity. The contributor's full name and affiliation may be found in the "Contributors" section at the back of the volume.

**Appendix.** Every user should explore the variety of succinct information supplied by the Appendix, which includes conversion factors, measurement tables, fundamental constants, and a biographical listing of scientists. Users wishing to go beyond the scope of this Encyclopedia will find recommended books and journals listed in the "Bibliographies" section; the titles are grouped by subject area.

**Index.** The 3500-entry index offers the reader the time-saving convenience of being able to quickly locate specific information in the text, rather than approaching the Encyclopedia via article titles only. This elaborate breakdown of the volume's contents assures both the general reader and the professional of efficient use of the McGraw-Hill Concise Encyclopedia of Chemistry.

### **CONTENTS**

Staffiv
Consulting Editors
Prefacevii
Organization of the Encyclopediaviii
<b>Articles, A–Z</b>
<b>Appendix</b>
Bibliographies
Equivalents of commonly used units for the U.S.
Customary System and the metric system
Conversion factors for the U.S. Customary System,
metric system, and International System
Defining fixed points of the International Temperature
Scale of 1990 (ITS-90)
Primary thermometry methods
Principal spectral regions and fields of spectroscopy
Recommended values (2002) of selected fundamental constants625
Electromagnetic spectrum
Standard atomic weights
Biographical listing
Contributors 637–647
Index 648–663



**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 a unit volume 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 waveguide 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.

In the chemical process industries and in related areas such as petroleum refining and fuels purification, absorption usually means gas absorption. This is a unit operation in which a gas (or vapor) mixture is contacted with a liquid solvent selected to preferentially absorb one, or in some cases more than one, component from the mixture. The purpose is either to recover a desired component from a gas mixture or to rid the mixture of an impurity. In the latter case, the operation is often referred to as scrubbing.

### 2 Accelerator mass spectrometry

When the operation is employed in reverse, that is, when a gas is utilized to extract a component from a liquid mixture, it is referred to as gas desorption, stripping, or sparging.

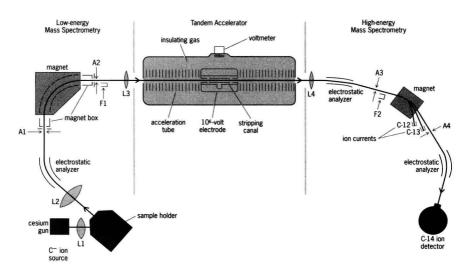
In gas absorption, either no further changes occur to the gaseous component once it is absorbed in the liquid solvent, or the absorbed component (solute) will become involved in a chemical reaction with the solvent in the liquid phase. In the former case, the operation is referred to as physical gas absorption, and in the latter case as gas absorption with chemical reaction. See Gas absorption operations; Unit operations.

[W.F.F.]

**Accelerator mass spectrometry** The use of a combination of mass spectrometers and an accelerator to measure the natural abundances of very rare radioactive isotopes. These abundances are frequently lower than parts per trillion. The most important applications of accelerator mass spectrometry are in archeological and geophysical studies, as, for example, in radiocarbon dating by the counting of the rare carbon-14 (radiocarbon; <sup>14</sup>C) isotope. See MASS SPECTROSCOPE.

The advantage of counting the radioactive atoms themselves rather than their decay products is well illustrated by radiocarbon dating, which requires the measurement of the number of <sup>14</sup>C atoms in a sample. The long half-life of 5730 years for <sup>14</sup>C implies that only 15 beta-particle emissions per minute are observed from 1 g of contemporary carbon. However, an accelerator mass spectrometer can be used to count the <sup>14</sup>C atoms at over 15 per second from a milligram sample of carbon. Consequently, accelerator mass spectrometry can be used to date samples that are a thousand times smaller than those that are dated by using the beta-particle counting method, and the procedure is carried out about 120 times faster.

For the study of many rare radioactive atoms, accelerator mass spectrometry also has the important advantage that there can be no background except for contamination with the species being studied. For example, significant interference with the beta-particle counting of radiocarbon from cosmic rays and natural radioactivity occurs for



Simplified diagram of an accelerator mass spectrometer used for radiocarbon dating. The equipment is divided into three sections. Electric lenses L1–L4 are used to focus the ion beams; apertures A1–A4 and charge collection cups F1 and F2 are used for setting up the equipment.

carbon samples about 25,000 years old. In contrast, accelerator mass spectrometer measurements are affected only by the natural contamination of the sample which becomes serious for samples about 50,000 years old.

**Apparatus.** The success of accelerator mass spectrometry results from the use of more than one stage of mass spectrometry and at least two stages of ion acceleration. The illustration shows the layout of an ideal accelerator mass spectrometer for radiocarbon studies, divided for convenience into three stages.

The first part of the accelerator mass spectrometer is very similar to a conventional mass spectrometer. In the second stage, a tandem accelerator first accelerates negative ions to the central high-voltage electrode, converts them into positive ions by several successive collisions with gas molecules in a region of higher gas pressure, known as a stripping canal, and then further accelerates the multiply charged positive ions through the same voltage difference back to ground potential. In the third stage, the accelerated ions are analyzed further by the high-energy mass spectrometer.

**Distinguishing features.** The features that clearly distinguish accelerator mass spectrometry from conventional mass spectrometry are the elimination of molecular ions and isobars from the mass spectrometry.

A tandem accelerator provides a convenient way of completely eliminating molecular ions from the mass spectrometry because ions of a few megaelectronvolts can lose several electrons on passing through the region of higher gas pressure in the stripping canal. Molecules with more than two electrons missing have not been observed, so that accelerator mass spectrometry utilizing charge -3 ions is free of molecular interferences.

The use of a negative-ion source, which is necessary for tandem acceleration, can also ensure the complete separation of atoms of nearly identical mass (isobars). In the case of radiocarbon analysis, the abundant stable <sup>14</sup>N ions and the very rare radioactive <sup>14</sup>C ions are separated completely because the negative ion of nitrogen is unstable whereas the negative ion of carbon is stable. In other cases, it is possible to count the ions without any background in the ion detectors because of their high energy. In many cases, it is also possible to identify the ion. See MASS SPECTROMETRY.

[A.E.L.]

**Acetal** A geminal diether ( $R_1 = H$ ). Ketals, considered a subclass of acetals, are also geminal diethers ( $R_1 = C$ , aliphatic or aromatic). Acetals are (1) independent structural units or a part of certain biological and commercial polymers, (2) blocking or protecting groups for complex molecules undergoing selective synthetic transformations, and (3) entry compounds for independent organic chemical reactions. See POLYACETAL.

Acetals are easily prepared by the reaction of aldehydes with excess alcohol, under acid-catalyzed conditions. This is usually a two-step process (see reaction below) in

which an aldehyde is treated with an alcohol to yield a less stable hemiacetal, which then reacts with additional alcohol to give the acetal. Protonic or Lewis acids are effective catalysts for acetal formation; dehydrating agents, such as calcium chloride and molecular sieves, can also be used for molecules, such as sugars, where acids may

### 4 Acetic acid

cause problems. Less common acetal preparations are Grignard reagent condensation with orthoformates and mercuric-catalyzed additions of alcohols to acetylenes. See ALDEHYDE; KETONE; ORGANIC SYNTHESIS. [C.F.B.]

**Acetic acid** A colorless, pungent liquid,  $CH_3COOH$ , melting at  $16.7^{\circ}C$  and boiling at  $118.0^{\circ}C$ . 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 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; WOOD CHEMICALS.

Pure acetic acid is completely miscible with water, ethanol, diethyl ether, and carbon tetrachloride, but is not soluble in carbon disulfide. In a water solution, acetic acid is a typical weakly ionized acid ( $Ka = 1.8 \times 10^{-5}$ ). 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. [F.W.]

**Acetone** A chemical compound,  $CH_3COCH_3$ . 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  $56.2^{\circ}C$  ( $133.2^{\circ}F$ ), melting point  $-94.8^{\circ}C$  ( $-138.6^{\circ}F$ ), and specific gravity 0.791.

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.

[D.A.S.]

**Acetylcholine** A naturally occurring quaternary ammonium cation ester, with the formula  $CH_3(O)COC_2H_4N(CH)_3^+$ , that plays a prominent role in nervous system function. The great importance of acetylcholine derives from its role as a neurotransmitter for cholinergic neurons, which innervate many tissues, including smooth muscle and skeletal muscle, the heart, ganglia, and glands. The effect of stimulating a cholinergic nerve, for example, the contraction of skeletal muscle or the slowing of the heartbeat, results from the release of acetylcholine from the nerve endings.

Acetylcholine is synthesized at axon endings from acetyl coenzyme A and choline by the enzyme choline acetyltransferase, and is stored at each ending in hundreds of thousands of membrane-enclosed synaptic vesicles. When a nerve impulse reaches an axon ending, voltage-gated calcium channels in the axonal membrane open and calcium, which is extremely low inside the cell, enters the nerve ending. The increase in calciumion concentration causes hundreds of synaptic vesicles to fuse with the cell membrane and expel acetylcholine into the synaptic cleft (exocytosis). The acetylcholine released at a neuromuscular junction binds reversibly to acetylcholine receptors in the muscle end-plate membrane, a postsynaptic membrane that is separated from the nerve ending by a very short distance. The receptor is a cation channel which opens when two acetylcholine molecules are bound, allowing a sodium current to enter the muscle cell and depolarize the membrane. The resulting impulse indirectly causes the muscle to contract.

Acetylcholine must be rapidly removed from a synapse in order to restore it to its resting state. This is accomplished in part by diffusion but mainly by the enzyme acetylcholinesterase, which hydrolyzes acetylcholine.

Acetylcholinesterase is a very fast enzyme: one enzyme molecule can hydrolyze 10,000 molecules of acetylcholine in 1 s. Any substance that efficiently inhibits acetylcholinesterase will be extremely toxic. [I.B.W.]

**Acetylene** An organic compound with the formula  $C_2H_2$  or  $HC \equiv CH$ . The first member of the alkynes, acetylene is a gas with a narrow liquid range; the triple point is  $-81^{\circ}C$  ( $-114^{\circ}F$ ). The heat of formation ( $\Delta H_f^{\circ}$ ) is +227 kilojoules/mole, and acetylene is the most endothermic compound per carbon of any hydrocarbon. The compound is thus extremely energy-rich and can decompose with explosive force. At one time acetylene was a basic compound for much chemical manufacturing. It is highly reactive and is a versatile source of other reactive compounds.

The availability of acetylene does not depend on petroleum liquids, since it can be prepared by hydrolysis of calcium carbide ( $CaC_2$ ), obtained from lime (CaO), and charcoal or coke (C). In modern practice, methane ( $CH_4$ ) is passed through a zone heated to  $1500^{\circ}C$  ( $2732^{\circ}F$ ) for a few milliseconds, and acetylene is then separated from the hydrogen in the effluent gas.

The main use of acetylene is in the manufacture of compounds derived from butyne-1,4-diol. The latter is obtained by condensation of acetylene with two moles of formaldehyde and is converted to butyrolactone, tetrahydrofuran, and pyrrolidone. Two additional products, vinyl fluoride and vinyl ether, are also based on acetylene.

Because of the very high heat of formation and combustion, an acetylene-oxygen mixture provides a very high temperature flame for welding and metal cutting. For this purpose acetylene is shipped as a solution in acetone, loaded under pressure in cylinders that contain a noncombustible spongy packing. See ALKYNE. [J.A.Mo.]

**Acid and base** Two interrelated classes of chemical compounds, the precise definitions of which have varied considerably with the development of chemistry. Some of these controversies are still unresolved.

Acids initially were defined only by their common properties as substances which had a sour taste, dissolved many metals, and reacted with alkalies (or bases) to form salts. For a time 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. This concept of an acid 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 alkalies, soda and potash, were the best-known bases, but it soon became clear that there were other bases, notably ammonia and the amines.

When the concept of ionization of chemical compounds in water solution became established, acids were defined as substances which ionized in aqueous solution to give hydrogen ions,  $H^+$ , and bases were substances which reacted to give hydroxide ions,  $OH^-$ . These definitions are sometimes known as the Arrhenius-Ostwald theory of acids and bases. Their use makes it possible to discuss acid and base equilibria and also the strengths of individual acids and bases.

A powerful and wide-ranging protonic theory of acids and bases was introduced by J. N. Brønsted in 1923 and was rapidly accepted. Somewhat similar ideas were advanced almost simultaneously by T. M. Lowry and the new theory is occasionally called the Brønsted-Lowry theory. The Brønsted definitions of acids and bases are: An

### 6 Acid anhydride

	Acids	Bases	Hall of
Strong acids	H <sub>2</sub> SO <sub>4</sub> HCI H <sub>3</sub> O <sup>+</sup> HSO <sub>4</sub> HF <sub>(aq)</sub> CH <sub>3</sub> COOH NH <sub>4</sub> *	HSO <sub>4</sub> <sup>-</sup> C1 C1 H <sub>2</sub> O SO <sub>4</sub> <sup>2</sup> F - CH <sub>3</sub> COO NH <sub>3</sub>	Weak bases
↓ Weak acids	NCO <sub>3</sub> <sup>-</sup> H <sub>2</sub> O C <sub>2</sub> H <sub>5</sub> OH	CO <sub>3</sub> <sup>2</sup> - OH- C <sub>2</sub> H <sub>5</sub> O-	Strong

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 (Arrhenius) 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 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 examples.

As the table shows, strengths of acids and bases are not independent. A very strong Brønsted acid implies a very weak conjugate base and vice versa. A qualitative ordering of acid strength or base strength 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.

Studies of catalysis have played a large role in the acceptance of a set of quite different definitions of acids and bases, those due to G. N. Lewis: 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. Bases under the Lewis definition are very similar to those defined by Brønsted, but the Lewis definition for acids is very much broader.

Another comprehensive theory 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 free electrons. Bases are similarly defined as substances which give up anions or electrons and add themselves to cations. So far, this theory has had little acceptance, quite possibly because the definitions are too broad to be very useful. See BASE (CHEMISTRY); BUFFERS (CHEMISTRY); HYDROGEN ION. [FA.L.; R.H.Bo.]

**Acid anhydride** One of an important class of reactive organic compounds derived from acids via formal intermolecular dehydration.

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.

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.

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 the reaction below.

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 glutaconic acids; and of aromatic 1,2-dicarboxylic acids, for example, phthalic acid. Commercially, however, both phthalic (structure 1) and maleic (2) 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.

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). 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. 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

### 8 Acid-base indicator

N-substituted and N,N-disubstituted amides, respectively. See ACID HALIDE; ACYLATION; CARBOXYLIC ACID; DIELS-ALDER REACTION; ESTER; FRIEDEL-CRAFTS REACTION. [P.E.F.]

**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.

Acid-base indicators are commonly employed to mark the end of an acid-base titration or to measure the existing pH of a solution. Care must be used to compare colors only within the indicator range. A color comparator may also be used, employing standard color filters instead of buffer solutions.

The indicator range is the pH interval of color change of the indicator. In this range there is competition between indicator and added base for the available protons; the color change, for example, yellow to red, is gradual rather than instantaneous. Observers may, therefore, differ in selecting the precise point of change.

Common-acid base indicators					
Common name	pH range	Color change (acid to base)	рК		
Methyl violet	0-2, 5-6	Yellow to blue violet to violet			
Metacresol purple	1.2–2.8, 7.3–9.0	Red to yellow to purple	1.		
Thymol blue	1.2-2.8, 8.0-9.6	Red to yellow to blue	1.		
Tropeoline 00 (Orange IV)	1.4-3.0	Red to yellow			
Bromphenol blue	3.0-4.6	Yellow to blue	4.		
Methyl orange	2.8-4.0	Orange to yellow	3.		
Bromcresol green	3.8-5.4	Yellow to blue	4.		
Methyl red	4.2-6.3	Red to yellow	5.		
Chlorphenol red	5.0-6.8	Yellow to red	6.		
Bromcresol purple	5.2-6.8	Yellow to purple	6.		
Bromthymol blue	6.0-7.6	Yellow to blue	7.		
Phenol red	6.8-8.4	Yellow to red	8.		
Cresol red	2.0-3.0, 7.2-8.8	Orange to amber to red	8.		
Orthocresol- phthalein	8.2-9.8	Colorless to red			
Phenolphthalein	8.4-10.0	Colorless to pink	9.		
Thymolphthalein	10.0-11.0	Colorless to red	9.		
Alizarin vellow GG	10.0-12.0	Yellow to lilac			
Malachite green	11.4-13.0	Green to colorless			

The table lists many of the common indicators, their ranges of pH and color change, and pK values. See ACID AND BASE; HYDROGEN ION; TITRATION. [A.L.H.]

**Acid halide** One of a large group of organic substances possessing the halocarbonyl group,

in which X stands for fluorine, chlorine, bromine, or iodine. The terms acyl and aroyl halides refer to aliphatic or aromatic derivatives, respectively.

The great inherent reactivity of acid halides precludes their free existence in nature; all are made by synthetic processes. In general, acid halides have low melting and boiling points and show little tendency toward molecular association. With the exception of the formyl halides (which do not exist), the lower members are pungent, corrosive, lacrimatory liquids that fume in moist air. The higher members are low-melting solids.

Acid chlorides are prepared by replacement of carboxylic hydroxyl of organic acids by treatment with phosphorus trichloride, phosphorus pentachloride, or thionyl chloride.

Although acid bromides may be prepared by these methods, acid iodides are best prepared from the acid chloride treatment with either  $CaI_2$  or HI, and acid fluorides from the acid chloride by interaction with HF or antimony fluoride.

The reactivity of acid halides centers upon the halocarbonyl group, resulting in substitution of the halogen by appropriate structures. Thus with substances containing active hydrogen atoms (for example, water, primary and secondary alcohols, ammonia, and primary and secondary amines), hydrogen chloride is formed together with acids, esters, amides, and *N*-substituted amides, respectively. [P.E.F.]

**Acrylonitrile** An explosive, poisonous, flammable liquid, boiling at 171°F (77.3°C), partly soluble in water. It may be regarded as vinyl cyanide, and its systematic name is 2-propenonitrile. Acrylonitrile is prepared by ammoxidation of propylene over various sorts of catalysts, chiefly metallic oxides.

Most of the acrylonitrile produced is consumed in the manufacture of acrylic and modacrylic fibers. Substantial quantities are used in acrylonitrile-butadiene-styrene (ABS) resins, in nitrile elastomers, and in the synthesis of adiponitrile by electrodimerization. Smaller amounts of acrylonitrile are used in cyanoethylation reactions, in the synthesis of drugs, dyestuffs, and pesticides, and as co-monomers with vinyl acetate, vinylpyridine, and similar monomers.

Acrylonitrile undergoes spontaneous polymerization, often with explosive force. It polymerizes violently in the presence of suitable alkaline substances. See NITRILE; POLYMERIZATION. [EW.]

**Actinide elements** The series of elements beginning with actinium (atomic number 89) and including thorium, protactinium, uranium, and the transuranium elements through the element lawrencium (atomic number 103). These elements have a strong chemical resemblance to the lanthanide, or rare-earth, elements of atomic numbers 57 to 71. Their atomic numbers, names, and chemical symbols are: 89, actinium (Ac), the prototype element, sometimes not included as an actual member of the actinide series; 90, thorium (Th); 91, protactinium (Pa); 92, uranium (U); 93, neptunium (Np); 94, plutonium (Pu); 95, americium (Am); 96, curium (Cm); 97, berkelium (Bk); 98, californium (Cf); 99, einsteinium (Es); 100, fermium (Fm); 101, mendelevium (Md); 102, nobelium (No); 103, lawrencium (Lr). Except for thorium and uranium, the actinide elements are not present in nature in appreciable quantities. The transuranium elements were discovered and investigated as a result of their synthesis in nuclear reactions. All are radioactive and except for thorium and uranium, weighable amounts must be handled with special precautions.

Most actinide elements have the following in common: trivalent cations which form complex ions and organic chelates; soluble sulfates, nitrates, halides, perchlorates, and sulfides; and acid-insoluble fluorides and oxalates. See ACTINIUM; LAWRENCIUM; PERIODIC TABLE; PROTACTINIUM; THORIUM; TRANSURANIUM ELEMENTS; URANIUM. [G.T.S.]

**Actinium** A chemical element, Ac, atomic number 89, and atomic weight 227.0. Actinium was discovered by A. Debierne in 1899. Milligram quantities of the element