# MIALL'S DICTIONARY OF CHEMISTRY

FIFTH EDITION

**DWA Sharp** 



## Miall's dictionary of chemistry

Edited by

D.W.A. Sharp

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LONGMAN GROUP LIMITED Longman House Burnt Mill, Harlow, Essex, UK

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First published 1940 Second edition 1949 Third edition 1961 Fourth edition 1968 Fifth edition 1981 ISBN 0 582 35152 9

Set in 8/9pt Monophoto Times

Printed in Great Britain by Richard Clay (The Chaucer Press) Ltd, Bungay Suffolk

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#### Preface to the fifth edition

In the fifth edition of this Dictionary I have tried to keep to the same principles that were adopted by my predecessors as editors, L. M. and S. Miall. I have aimed to provide an explanation of the terms used in the various branches of chemistry together with brief accounts of important substances, chemical operations and chemists themselves. The Dictionary is intended for use in schools, colleges and universities, for teaching, law, medicine, journalism, engineering and management where chemical terms may be encountered; but I hope that professional chemists will also find the definition of terms and description of areas outside of their speciality of use. We have necessarily had to be selective rather than comprehensive but I would appreciate receiving note of important omissions.

In this Edition we again have paid particular attention to industrial processes and have tried to give rather more indication of the use of particular chemicals. In order to give some idea of the relative magnitudes of production we have included data on annual production. In this, because of availability of data, we have not been entirely consistent in including common data or common units but we hope that these data will be of considerable use. (World, U.S. or European production figures are used as seem most appropriate or up-to-date – and it must be remembered that for most speciality chemicals U.S. production is dominant.)

The list of contributors is on page v and I am deeply indebted to them for it is they who have prepared this new Edition. Errors and omissions are my responsibility and I would appreciate receiving notice of them.

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### Abbreviations and nomenclature

Abbreviations and symbols commonly used in this book include:

A Angstrom unit \*
at.no. atomic number
at.wt. atomic weight
b.p. boiling point
Btu British thermal unit
d relative density

D-, DL- see optical activity, chirality

E energy

Gibbs function (see Gibbs free energy, free energy)

g gram

h Planck's constant\*

H enthalpy

L- see optical activity, chirality

lbs. pounds
M molar
M (in formulae) any metal
ml millilitre
mol.wt. molecular weight
m.p. melting point
L Avogadro's number\*

nm nanometres p.a. per annum

pH see hydrogen ion concentration

R gas constant\*

R gas constant\*

see ontical activ

R see optical activity, chirality

rH see rH
S entropy\*

s see optical activity, chirality

X (in formulae) any non-metal (usually a halogen)

 $\mu$  micron frequency

(+)- and (-)- see optical activity, chirality

For simple compounds the main reference uses the systematic I.U.P.A.C. nomenclature, but other nomenclature

is cross-referenced to the systematic name.

Note the symbol \* is used for cross-referencing throughout.

#### A

AAS Atomic absorption spectroscopy\*.

Abel, Frederick A. (1827–1902) British explosives chemist. Abel developed a method for the safe manufacture of guncotton. With Sir James Dewar he invented cordite.

Abel flash point See flash point.

abherents, release agents, parting agents Liquid or solid films which reduce or prevent adhesion between surfaces; solid-solid, solid-paste, solid-liquid. Waxes, metallic soaps, glycerides (particularly stearates), polyvinyl alcohol, polyethene, silicones, and fluorocarbons are all used as abherents in metal, rubber, food, polymer, paper and glass processing.

abietic acid, C20H30O2. A crystalline diterpenoid

acid obtained from pine rosin by acid treatment, which causes isomerization of primary resin acids (palustric, laevopimaric, neoabietic) to abietic acid, m.p. 172–175°C. The commercial product may be glassy and of low m.p. Used extensively in the manufacture of plastics, paints, varnishes, paper sizes and detergents.

ab-initio calculations Quantum mechanical calculations using the Schrödinger wave equation, which do not rely upon any experimental data for solution.

ablation Erosion and disintegration due to heat. Ablation-resistant materials, particularly Nylon fibres in a phenolic resin, are used to protect space vehicles during re-entry into the atmosphere. Decomposition to gaseous products with a porous refractory residue is desirable.

abrasives Hard materials used to disintegrate other materials. Amongst those most widely used are SiC, Al<sub>2</sub>O<sub>3</sub> (often containing Ti), diamond, tungsten carbides, BN, and metal abrasives, e.g. steel wool.

**abrin** A toxic substance, causing agglutination of the red blood corpuscles, found in the seeds of *Abrus precatorius*, an Indian shrub. It is a mixture of two proteins.

**absolute temperature** A temperature on the absolute or Kelvin scale usually denoted by T; the zero of this scale is the temperature at which a perfect

gas would occupy zero volume if it could be cooled indefinitely without liquefaction or solidification. The absolute zero  $(0\,\mathrm{K})$  is  $-273\cdot16^\circ\mathrm{C}$ , and one degree absolute is equivalent to one degree Centigrade;

$$T(K) = temperature (°C) + 273.16.$$

**absorptiometer** An instrument used to measure the absorption of light by a liquid. Also the name of the apparatus used to determine the solubility of a gas in a liquid.

absorption See gas absorption.

absorption bands See absorption of light.

absorption coefficient of a gas The volume of gas measured at 0°C and 760 mm pressure which will dissolve in 1 ml of a liquid. The absorption coefficients in water at 0°C for several common gases are as follows: N<sub>2</sub>, 0·024; O<sub>2</sub>, 0·049; C<sub>2</sub>H<sub>4</sub>, 0·25; CO<sub>2</sub>, 1·71; H<sub>2</sub>S, 4·68; SO<sub>2</sub>, 79·8; HCl, 506; NH<sub>3</sub>, 1300.

absorption coefficient of light See Lambert's law and Beer's law.

absorption column, absorption tower The equipment normally used for absorption of gases consists of a column or tower, usually circular in cross-section, the absorbing liquid passing down counter-current\* to the gas passing upwards. The two most important types of column are the plate\* or tray column and the packed column\*, although spray columns\* and others are sometimes used. In each case the object is to provide the maximum gas—liquid interfacial area with the minimum resistance to flow.

When the main object of the absorption is to remove impurities these columns are often referred to as scrubbers\*. See also wetted-wall absorber.

absorption of light When light falls on the surface of a transparent substance part of the light is reflected, the remainder is transmitted unchanged. If, however, the light falls upon the surface of a black substance, e.g. lampblack, it is neither reflected nor transmitted; all wavelengths are absorbed in a general absorption process. Many substances appear coloured because they have absorbed selectively all the wavelengths of white light except those corresponding to the particular colour which they appear. If the spectrum of the light transmitted by a coloured substance is examined it is found that certain wavelengths, called absorption bands, are missing. For gases in the atomic state the spectrum of the transmitted light shows dark lines rather than bands. These absorption lines correspond to the wavelengths of light absorbed by the atoms.

Relationships between the intensity of incident light, sample thickness, concentration and intensity of transmitted light are embodied in Beer's law\* and Lambert's law\*.

**absorption spectroscopy** Any spectroscopic technique, qualitative or quantitative, depending upon the measurement of an absorption spectrum.

1

#### absorption tower

absorption tower See absorption column.

ABS plastics A group of plastic materials based on blended copolymers of styrene-acrylonitrile (70:30) and butadiene-acrylonitrile (65:35) and on graft interpolymers of styrene and acrylonitrile with polybutadiene. Such plastics, although more expensive than for instance polystyrene, are very tough and of pleasing appearance although generally opaque. Used in pipe (25%), appliances (20%), and automotive parts (15%). U.S. consumption 1979 530 000 tonnes.

Ac Actinium. Also used for acetate (ethanoate).

acac Abbreviation for acetylacetonato group.

acacia See gum acacia.

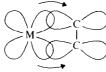
acaroid resin A gum from a tropical tree containing a mixture of coumaric acid, cinnamic acid and benzoic acid and their esters. A resin used in the manufacture of pyrotechnic compositions.

accelerators Substances used to accelerate desired cross-linking reactions in polymers. In particular they assist the vulcanization\* of rubber, in some cases conferring on it increased resistance to wear. Many types of organic compounds can be used and are classed as ranging from slow to fast accelerators. Of these for example, diphenylguanidine\* is medium fast, the thiazoles, e.g. mercaptobenzthiazole\*, are fast, and the thiuram disulphides\*, e.g. the tetramethyl derivatives, are ultrafast. The term is also used for those substances which act as catalysts by increasing the rate at which thermosetting resins cure or harden.

acceptor A substance which, while normally not oxidized by oxygen or reduced by hydrogen, can be oxidized or reduced in presence of a substance which is itself undergoing oxidation or reduction.

Also an atom, molecule, or ion that is electron deficient and which can form a co-ordinate link\* with an electron donor. Thus in the complex ion  $[Co(NH_3)_6]^{3+}$  the cobalt(III) ion is an acceptor and the ammonia the electron donor.  $\pi$ -acceptors are molecules or atoms which accept electrons into  $\pi$ , p or d orbitals.





 $\sigma$  bond (acceptor)

 $\pi$  bond (acceptor)

acenaphthene, C<sub>12</sub>H<sub>10</sub>. Colourless needles, m.p.

95 C, b.p. 278 C. When passed through a redhot tube acenaphthylene is obtained. Oxidation with acid dichromate gives naphthalic acid. Occurs in the anthracene fraction of coal tar, from which it is readily separated. Can be obtained synthetically by the action of KOH/EtOH on α-bromoethylnaphthalene.

It is important as a dyestuff intermediate, being much used as a source of nitro- and amino-derivatives.

acenaphthenequinone, C<sub>12</sub>H<sub>6</sub>O<sub>2</sub>. Yellow needles,

mp. 261°C. It is condensed with thioindoxyl and its derivatives to bright scarlet and red vat dyes.

acenaphthylene,  $C_{12}H_8$ . Crystallizes in yellow

plates from alcohol, m.p. 92-93°C (decomp.). It is derived from acenaphthene by catalytic dehydrogenation and polymerizes to give plastic products.

acetal, C<sub>0</sub>H<sub>14</sub>O<sub>2</sub>, CH<sub>3</sub>·CH(OEt)<sub>2</sub>. A pleasantsmelling liquid, b.p. 104–105°C, partially soluble in water and miscible with alcohol and ether. Prepared by mixing ethanal and ethanol in the presence of a catalyst, such as HCl, or by passing C<sub>2</sub>H<sub>2</sub> into EtOH in the presence of a catalyst. Used in the preparation of derivatives, some of which are useful solvents.

acetaldehyde See ethanal.

acetal resin See aldehyde polymers.

acetals Compounds of the general formula:

$$R^3$$
  $OR^1$ 
 $R^4$   $OR^2$ 

Derived from an aldehyde or ketone and an alcohol using an acid catalyst. Ethylene glycol or 1,3-dihydroxypropane are frequently used to give 5-or 6-member cyclic products.

acetamide See ethanamide.

acetanilide, C<sub>8</sub>H<sub>9</sub>NO, PhNH•CO•CH<sub>3</sub>. White crystals, m.p. 114°C. Very sparingly soluble in cold, more so in hot water, readily soluble in ethanol, ether, and chloroform.

Acetanilide is manufactured by reacting aniline with excess ethanoic acid or ethanoic anhydride. Formerly used medicinally, as an antipyretic and analgesic, but chief use is in the manufacture of dye intermediates such as *p*-nitroacetanilide,

p-nitroaniline and p-phenylenediamine. Also used in the manufacture of rubber, and as a peroxide stabilizer.

Hydrolysed by dilute acids and alkalis to aniline. It chlorinates more slowly than aniline to o-and p-chloroacetanilides.

acetate fibres See cellulose acetate.

acetates Salts or esters of ethanoic acid \*.

acetazolamide, S-acetamido-1,3,4-thiadiazole-2-sulphonamide,  $C_4H_6N_4O_3S_2$ . Crystals, sparingly

$$H_3C \cdot CO \cdot NH$$
 $S$ 
 $SO_2 \cdot NH_2$ 

soluble in cold water, m.p. 258°C. An inhibitor of carbonic anhydrase, the enzyme which catalyses the attainment of equilibrium in the reaction:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

it acts as a diuretic. Also used to treat glaucoma since it reduces the rate of formation of the aqueous humour filling the anterior chamber of the eye.

acetic acid See ethanoic acid.

acetic anhydride See ethanoic anhydride.

acetic ester, acetic ether, CH<sub>3</sub>C(O)O•C<sub>2</sub>H<sub>5</sub>. See ethyl ethanoate.

acetins Acetates (ethanoates) of glycerol. There are five possible acetates, two mono-, two di-, and one tri-acetate. Only four of these have been prepared in the pure state; the commercial acetins are mixtures of the various acetates and form colourless or slightly brown syrupy liquids.

Monoacetin, b.p.  $130-132^{\circ}C/2-3$  mm, contains chiefly the 1-acetate

CH<sub>2</sub>OH·CHOH·CH<sub>2</sub>OOCCH<sub>3</sub>. It is very soluble in water, not precipitated out of solution by NaCl; soluble in chloroform, but not very soluble in ether. Prepared by heating molecular proportions of glycerol and ethanoic acid with sulphuric acid, or by heating triacetin with glycerol. Used as a solvent for the dyes employed in printing paper bags.

Diacetin, b.p. 259°C is chiefly the 1:3-diacetate CH<sub>2</sub>OOCCH<sub>3</sub>·CHOH·CH<sub>2</sub>OOCCH<sub>3</sub>. Soluble in water and alcohol. Obtained as a by-product in the manufacture of triacetin. Used as plasticizer for cellulose acetate lacquers and as a solvent for basic dyes.

Triacetin, b.p. 260°C, is about 90% glycerol triacetate and 10% diacetate. Slightly soluble in water; soluble in ether. Prepared by heating glycerol with a large excess of ethanoic acid and extracting the triacetin from aqueous solution with ether. Used as a plasticizer for lacquers and as a solvent for certain gums and resins.

acetoacetanilide, C<sub>10</sub>H<sub>11</sub>NO<sub>2</sub>,

PhNH-CO-CH<sub>2</sub>COCH<sub>3</sub>. M.p. 85°C. Prepared by the action of acetoacetic ester on aniline. Used

for the preparation of pigment dyestuffs by coupling with diazotized bases.

acetoacetic acid, acetonemonocarboxylic acid, butan-3-onoic acid, C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>, CH<sub>3</sub>CO·CH<sub>2</sub>COOH. A colourless and strongly acid syrup. It is unstable, and decomposes into propanone and carbon dioxide below 100°C. Prepared from acetoacetic ester. It occurs in traces in normal urine, but is characteristically present in increased amount in the urine of diabetic patients. Aqueous solutions of the acid give a distinctive violet colour with FeCl<sub>3</sub>.

acetoacetic ester See ethyl acetoacetate.

acetogenins See polyketides.

acetoin, acetyl methyl carbinol, 3-hydroxy-2-butanone,  $C_4H_8O_2$ ,  $CH_3CH(OH)COCH_3$ . M.p. 15°C, b.p. 148°C. Miscible with water and alcohol; insoluble in ether. Produced from propene and butene glycols by the action of ethanoic acid bacteria, and from ethanal by yeast. Prepared by the reduction of diacetyl(2,3-butanedione). When distilled, it forms diacetyl.

acetol See hydroxypropanone.

acetolysis The process of removing acetyl groups from an organic compound. It is usually carried out by heating the acetyl compound with aqueous or alcoholic alkalis, whereby the acetyl groups are removed as ethanoic acid.

acetone See propanone.

acetone alcohol See hydroxypropanone.

acetone bodies See ketone bodies.

acetone dicarboxylic acid,  $\beta$ -ketoglutaric acid,  $C_5H_6O_5$ , CO·(CH<sub>2</sub>COOH)<sub>2</sub>. Colourless needles, m.p. 135°C (decomp.). Soluble in water and alcohol; insoluble in benzene and chloroform. Prepared by the action of sulphuric acid on citric acid. Readily decomposed by boiling water, acids, or alkalis to acetone (propanone) and carbon dioxide. Gives a violet colour with FeCl<sub>3</sub> and a white precipitate with HgSO<sub>4</sub>. The acid or its diethyl ester reacts with sodium in a manner similar to acetoacetic ester. The ester is used in organic syntheses.

acetone monocarboxylic acid See acetoacetic acid.

acetonitrile, methyl cyanide, ethanenitrile, CH<sub>3</sub>CN. Poisonous liquid, b.p. 82°C, miscible with water and many organic solvents. Prepared from ethyne and ammonia or by dehydration of ethanamide. Widely used for dissolving inorganic and organic compounds, especially when a non-aqueous polar solvent of high dielectric constant is required, e.g. for ionic reactions.

acetonyl The group CH<sub>3</sub>COCH<sub>2</sub>-.

acetonylacetone See hexan-2,5-dione.

 almonds. Insoluble in water, miscible in all proportions with alcohol, ether, and benzene. Occurs in coal tar. Prepared by the action of ethanoyl chloride upon benzene in the presence of aluminium chloride. Has typical ketonic properties. Oxidized by potassium permanganate to phenylglyoxylic acid. Used as a solvent for cellulose ethers.

acetoxy The group CH<sub>3</sub>COO-.

acetylacetonates Metal derivatives of acetyl-

acetone generally containing the grouping shown (Macae) with some delocalization in the ring. In some derivatives (e.g. Pt) the metal is bonded to the central carbon atom. The number of acetylacetonate groups bonded to the metal can vary from 1 to 4.

acetylacetone, C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, CH<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>. A diketone with enolic properties. The enolate ion acac forms stable complexes with many metals, e.g. tris(acetylacetonato)iron(III), Feacac<sub>3</sub>. Metal derivatives are generally soluble in organic solvents and often appreciably volatile; they are used in solvent extraction and mass spectrometry. Derivatives of acetylacetone, e.g.

CF<sub>3</sub>COCH<sub>2</sub>COCH<sub>3</sub>, CF<sub>3</sub>COCH<sub>2</sub>COCF<sub>3</sub> and thienylCOCH<sub>2</sub>COCF<sub>3</sub> form particularly stable derivatives.

acetylation, ethanoylation A process for introducing acetyl groups into an organic compound containing -OH, -NH<sub>2</sub> or -SH groups. It is carried out by heating the compound with ethanoic anhydride or ethanoic chloride usually in presence of an inert solvent such as benzene or ethanoic acid. In many cases, zinc chloride or pyridine is used to hasten the reaction.

acetyl chloride See ethanoyl chloride.

acetylcholine, C<sub>7</sub>H<sub>17</sub>NO<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>OOCCH<sub>3</sub>OH<sup>-</sup>. Held in synaptic vesicles in the nerve endings between nerves and the voluntary, skeletal muscles and also between parts of the parasympathetic system and some involuntary muscle cells. Passage of a nerve impulse from a nerve end to another nerve or muscle cell causes release of acetylcholine to transmit the impulse across the intercellular space. Receptor sites receive the acetylcholine and combination causes a depolarization of the receiving cell membrane, initiating another impulse. The acetylcholine is quickly destroyed by the hydrolytic action of acetylcholine esterase, which is also found in the intercellular spaces. Injection of acetylcholine can cause dilatation of the arteries and a rapid fall in blood pressure at a dilution of one part in ten millions. Many drugs interfere either with acetylcholine or its destruction by the esterase, thus blocking transmission across synapses, e.g. nicotine, curare and some nerve gases.

acetyl coenzyme A A reactive thioester of fundamental importance in metabolism and biosynthesis. The acetyl group is bound to the thiol group of coenzyme A\*, and its high reactivity is reflected in the term 'active acetate'. Acetyl coenzyme A is the principal substrate of the citric acid cycle\*. It also acts as an acetylating agent, e.g. in the formation of acetylcholine. It has a central role in three major biosynthetic pathways: (1) formation of fatty acids from acetyl coenzyme A and malonyl coenzyme A (itself arising by carboxylation of acetyl coenzyme A), (2) synthesis of the polyketides via acetoacetyl coenzyme A, (3) synthesis of the terpenoids and steroids via mevalonic acid.

acetylene See ethyne.

acetylene black, cuprene A form of carbon black prepared by pyrolysis of ethyne.

**acetylene complexes** Co-ordination compounds similar to olefin complexes \*.

acetylene dicarboxylic acid,  $HO_2CC \equiv CCO_2H$ . See dimethylacetylenedicarboxylate.

acetylene dichloride See dichloroethylenes.

acetylene tetrachloride See sym tetrachloroethane.

acetylides Carbides\* containing C<sub>2</sub><sup>2-</sup> or C<sub>2</sub>H<sup>-</sup> species. Formed by more electropositive elements (e.g. K, Ca, Al) and by some transition elements (e.g. Cu, Ag, Au). Hydrolysed to ethyne, C<sub>2</sub>H<sub>2</sub>. Most transition metal acetylides are explosive.

Metal derivatives of terminal acetylenes,  $RC_2H$ . Transition metals form complex acetylides (e.g.  $[M(C \equiv CR)_n]^{x-}$ ) often containing the metal in low oxidation states.

acetyl radical The radical CH<sub>3</sub>CO· formed in the free state during the photolysis of propanone. It is dissociated above 60°C into CO and CH<sub>3</sub>. Acetyl derivatives contain this group.

acetyl value The acetyl value of a fat is the number of milligrams of potassium hydroxide required to neutralize the ethanoic acid liberated when 1g of acetylated fat is saponified. It is a measure of the number of free hydroxyl groups in the fat.

Acheson, Edward G. (1856–1931) U.S. industrial chemist. After working with Edison on the development of electric lamps, Acheson discovered silicon carbide (carborundum) in 1891. He then established a company for the manufacture of carborundum and synthetic graphite using electric furnaces. Acheson also developed lubricants based on colloidal graphite (oildag and aquadag).

achiral The molecule of a compound which is not optically active \* is achiral.

achromatic indicators Substances which give a

grey end-point and generally find application in the titration of turbid liquids.

acid An acid on the aqueous system is defined as a substance which is capable of forming hydrogen ions when dissolved in water. Most inorganic acids may be regarded as a compound of an acidic oxide and water; where the oxide concerned is that of a metal, that oxide may exhibit amphoteric character, that is act sometimes as an acid and sometimes as a base. Aqueous solutions of acids have a sharp taste, turn litmus red, liberate carbon dioxide from a metallic carbonate and give reactions characteristic of the anion present.

Since free protons cannot exist, acidic properties can only be shown when the solvent can act as a proton acceptor, i.e. as a base. Thus aqueous solutions of acids contain the hydroxonium ion, H<sub>3</sub>O<sup>+</sup>. Acids can also exist in non-aqueous solvents. Since ammonia can also solvate a proton to give the ammonium ion, NH<sub>4</sub>+, substances which dissolve in ammonia to give the ammonium ion, e.g. NH<sub>4</sub>Cl, are acids in that system.

Liquid water is ionized

$$2H_2O = H_3O^+ + OH^-$$

this ionization being the reverse of the neutralization reaction in water; substances giving hydroxyl ions are bases in water. Liquid ammonia is ionized

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

and amides are bases on this system.

The concept of acids and bases has been extended to solvents which are ionized and yet do not contain hydrogen: a substance giving the appropriate positive ion is an acid on that system. Thus bromine trifluoride ionizes

$$2BrF_3 \Longrightarrow BrF_2^+ + BrF_4^-$$

and a substance giving the BrF<sub>2</sub><sup>+</sup> ion in solution, e.g. BrF<sub>3</sub>·SbF<sub>5</sub>, is an acid in the system.

Typical organic acids contain the -C(O)OH group, but many other acid groupings, e.g. the sulphonic -S(O)<sub>2</sub>OH give acidic properties to organic compounds. Phenols have acidic properties and are classified with enols as pseudo-acids.

The term acid was extended by Lewis to include substances which are electron acceptors. Thus AlCl<sub>3</sub> can accept electrons from a chloride ion forming the [AlCl<sub>4</sub>]<sup>-</sup> ion and is a Lewis acid.

The 'strength' of an acid is measured by the

The 'strength' of an acid is measured by the value of its dissociation constant, 'strong' acids, e.g. HCl, HNO<sub>3</sub>, being substantially fully ionized in solution and 'weak' acids predominately unionized.

acid-base indicator A substance, a weak acid or weak base, which has a different colour in acid or base solution. The colour change is due to a marked difference in colour between the undissociated and ionic forms. For a good indicator the colour change must occur between narrow limits of pH, e.g. methyl orange is red at pH 3·1 and changes to yellow at pH 4·4.

acid dyes Dyestuffs containing an aromatic chro-

mophoric group and a group conferring solubility in water, generally the SO<sub>3</sub>H group as its sodium salt. They are relatively simple in application. The types of acid dyestuffs are:

Simple acid dyes contain no polyvalent metals and are not improved by after treatment with Na<sub>2</sub>Cr<sub>2</sub>O<sub>2</sub>/dil. HCl.

Mordant acid dyes combine simultaneously with the mordanting agent (generally Cr(OH)<sub>3</sub>) and the fibre; the dyestuff generally contains ortho OH-azo or OH-OH groups.

Premetallized acid dyes are similar to the simple acid dyes but are already complexed to a metal.

acid egg A non-mechanical pump for the handling of highly corrosive liquids. Liquid is admitted to a corrosion-resistant vessel and forced into the delivery line by compressed air.

acid exchange resins See ion exchange.

acid oil The name sometimes given to the alkali extract of phenol derivatives formed in the production of gasoline by cracking operations. Also referred to as cresylic acids\* or 'phenols'.

acid sludge A complex acid residue produced when kerosines, lubricating oils or other petroleum products are refined with sulphuric acid or oleum. It consists of hydrocarbons, sulphonic acids and free sulphuric acid. Petroleum sulphonates can be recovered by extraction with alkali followed by further refining and are used as anionic agents in the 'oil-in-water' emulsions for the metal processing, textile and leather industries.

acid (steel or process) Refers to the nature of the slag in steel production.

acid tar See acid sludge.

acid value, acid number An empirical measure of the free titratable acid content of a substance, defined as the mg KOH required to neutralize 1 g of substance using phenolphthalein as indicator. The term is used for fats, oils, resins, plasticizers and solvents. See neutralization value.

acitrizoic acid, C<sub>9</sub>H<sub>6</sub>I<sub>3</sub>O<sub>3</sub>. White powder, slightly

soluble in water and in the alkali hydroxides. Solutions of the sodium salt and preferably the sodium salt of diatrizoic acid, 3,5-diacetamido-2,4,6-triiodobenzoic acid are used as X-ray contrast media. They are injected intravenously and used to outline the renal system.

**aconitic acid,**  $C_6H_6O_6$ . Generally the *trans* acid, m.p. 194 C (decomp.). It can be prepared by dehydrating citric acid with  $50^\circ_0$  sulphuric acid. Present in cane molasses. (See diagram on next page.)

The cis form has m.p. 125°C and is converted into the trans form on heating.

**aconitine** Intensely poisonous alkaloid obtained from *Aconitum napellus*, monksbane, m.p. 197°C. Its structure is related to delphinine.

acridine, C<sub>13</sub>H<sub>9</sub>N. Colourless needles, m.p.

111°C. It is soluble in alcohol and sparingly soluble in hot water. It occurs in the high-boiling fraction of coal tar.

acriflavine A mixture of 2,8-diamino-10-methylacridinium chloride hydrochloride, and 2,8-diaminoacridine dihydrochloride. It may be prepared by partially quaternizing diacetyldiaminoacridine and hydrolysing the product with hydrochloric acid. It is a red crystalline powder, soluble in water and alcohol, but insoluble in chloroform. It is used for the same purposes as proflavine\*.

**Acrilan** A brand name for a synthetic fibre, based on a copolymer of acrylonitrile with minor proportions of other unspecified vinyl monomers. *See also* propenenitrile.

acrolein See propenal.

acrolein polymers, propenal polymers Polymers of  $CH_2 = CHCHO$  generally formed by free radical polymerization. Polymerization is generally through the vinyl group and the aldehyde groups are present as acetals. Polymerization with strong base causes polymerization through the carbonyl group. Acrolein polymers can be modified chemically and used as thickening agents and protective colloids. Also used in plastics and lacquers. Disacryl is an insoluble acrolein polymer.

acrylamide polymers See polyacrylamide.

acrylic acid See propenoic acid.

acrylic acid polymers Acrylic acid,

CH<sub>2</sub>=CHCO<sub>2</sub>H, and methacrylic acid, CH<sub>2</sub>=CMeCO<sub>2</sub>H undergo free radical polymerization to give polymers used as thickeners, in textile treatment, as drilling-mud additives, as floculating agents, in paper making, and if co-polymerized with e.g. divinylbenzene as ion-exchange resins

acrylate resins and plastics Generally used to refer to polymeric methyl acrylate (methyl propenoate) and polymeric methyl methylacrylate (methaccrylate) (methyl 2-methyl propenoate). Polymeric methyl acrylate is used, principally in an emulsion form, in textile and leather finishes, lacquers,

paints, adhesives and safety glass interlayers. Polymeric methyl methylacrylate gives a clear solid material (Perspex) and is used in injection moulding and extrusion. U.S. production 1978 330 000 tonnes

acrylonitrile See propenenitrile.

acrylonitrile polymers See polyacrylonitrile.

ACTH Adrenocorticotropic hormone\*.

actin See actomyosin.

actinides The elements actinium, thorium, protactinium, uranium, neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium are collectively known as actinides. Those with atomic numbers 93 and above are artificial and are produced by irradiation of uranium or other artificial elements with neutrons, alpha particles, or carbon or nitrogen ions. In the actinide elements the 5f shell is being filled and they are thus analogous to the lanthanides or rare-earth elements. There is less shielding of the 5f electrons than of the 4f and valencies greater than three are common, particularly among lighter members of the series. Amongst the heavier elements the +2 state becomes stable.

All of the actinides are radioactive and present some health hazards; with the more radioactive elements all handling has to be by remote control and no contact with the operator is permissible.

actinium, Ac. At.no. 89, m.p.  $1050^{\circ}$ C, b.p.  $3200 \pm 300^{\circ}$ C. Occurs naturally as a minor constituent in uranium ores but difficult to separate and best prepared by bombardment of radium with neutrons. Separated from other species by ion exchange or solvent extraction. The most stable isotope <sup>227</sup>Ac is very radioactive ( $t_{\frac{1}{2}}$  22 years), the metal glows blue and is oxidized in air. It has been prepared by reduction of AcF<sub>3</sub> with lithium vapour at  $1200^{\circ}$ C and is silvery white in colour.

actinium compounds Because of its intense radioactivity very few actinium compounds have been isolated. In its compounds the element is tripositive, forming very similar compounds to lanthanum\*. Actinium salts are colourless.

**actinometer** A device which determines the intensity of a beam of radiation.

actinon An obsolete name for radon \*.

activated adsorption There are two types of adsorption; in one the association is physical and in the other chemical. Physical adsorption is the more common and involves van der Waals forces of attraction between the two phases. Chemical adsorption (chemisorption) involves the formation of chemical bonds between the two phases. Since chemisorption often has an activation energy associated with it, it is sometimes referred to as activated adsorption.

activated carbon See active carbon.

activated clay A natural clay or earth pretreated with acid and used, for example, to remove reaction products and acid sludge\* from acid-treated oils.

activated molecule Molecules will only react on collision when they possess more than a certain minimum amount of energy. A molecule which has acquired more energy than the average amount possessed by other molecules, and is therefore in a more reactive condition, is said to be activated. Molecules are activated when they absorb a quantum of light, or after coming in contact with a hot surface.

activation analysis An analytical technique in which an artificial radioactive isotope is formed by irradiation (generally with neutrons) from the stable element to be determined and the amount of the artificial isotope is then estimated from its radioactivity.

activation energy The minimum energy which reacting species must possess in order to be able to form an 'activated complex' or transition state before proceeding to the products. The activation energy  $(E_a)$  may be derived from the temperature dependence of the reaction rate using the Arrhenius equation \*.

active carbon Carbon (charcoal) treated at high temperature with steam, air or CO<sub>2</sub>, the process removing hydrogen from the surface and also opening up capillaries. It is an excellent adsorbent for removal of small traces of impurities from a gas or liquid and is very specific the adsorption also taking place at low relative pressures. Used extensively in water and waste water treatment, air pollution control, as a catalyst, sugar refining, purification of chemicals and gases (gas masks), dry cleaning, rubber reclamation, cigarette filters. U.S. production 90 000 tonnes p.a.

active centres In heterogeneous catalysis it is generally agreed that the chemisorption of at least one of the reactants is a necessary prerequisite to catalysis. In 1925 H. S. Taylor proposed that the amount of the catalyst surface which was active for catalysis depended upon the reaction which was being catalysed, and that the adsorption occurred at active centres on the surface of the catalyst. Evidence for the existence of active centres is obtained from the observation that the adsorption of small amounts of foreign substances, much less than that required for monolayer coverage, can often completely poison the catalyst. The concept of active centres has been extended to enzymes and bacterial action.

active earths See bleaching earths.

active mass An old term used to express the influence of concentration of a substance on the position of equilibrium in a reversible chemical reaction (see mass action, Law of). The active mass is represented exactly by the thermodynamic activity\*.

active transport The biochemical transport of substances, usually against a concentration gradient, other than by osmosis or diffusion. It requires energy, usually supplied as ATP, and is essential to many physiological processes such as the transport of the ions Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>. Glucose is actively transported into cells and amino acids are reabsorbed by kidney tubules in a similar manner.

activity A thermodynamic quantity which measures the effective concentration or intensity of a particular substance in a given chemical system. The absolute activity,  $a^{\circ}$ , of a substance is given by  $\mu = RT \ln a^{\circ}$ , where  $\mu$  is the chemical potential\* of the substance, R is the gas constant, T the absolute temperature. The relative activity, a, is given by  $\mu = \mu^{\circ} + RT \ln a$ ;  $\mu^{\circ}$  being the chemical potential of the substance in its standard state\*. For dilute, ideal solutions the activity is directly proportional to the concentration; for ideal gases, activity is proportional to the partial pressure of the gas.

activity coefficient  $(f \text{ or } \gamma)$  A dimensionless factor by which the concentration (c) of a substance must be multiplied to give an exact measure of its thermodynamic activity (a) in a chemical system, i.e. a = fc. It is a measure of the deviation from ideal behaviour of the solution; f is unity for an ideal mixture and greater or less than unity for a non-ideal system. Activity coefficients of electrolytes are considered to be the geometrical mean of the single ion activities, the latter being hypothetical quantities which cannot be determined separately.

activity series The elements arranged in order of their electrode potentials \*.

actomyosin The most important protein of muscle, made up of two separate proteins actin and myosin. Actomyosin is insoluble in water but gives viscous solutions with neutral salts. Muscle appears to act by filaments of actin sliding between filaments of myosin.

**acyclic** See aliphatic. Containing chains, possibly with branches but no rings.

acyl The general name for organic acid groups, which are the residues of carboxylic acids after removal of the -OH group, e.g. acetyl chloride, CH<sub>3</sub>CO·Cl, is the acyl chloride formed from acetic acid, CH<sub>3</sub>CO·OH, or, using I.U.P.A.C. nomenclature ethanoyl chloride from ethanoic acid. The names of the individual acyl groups are formed by replacing the -ic of the acid by -yl.

**acylation** A chemical transformation which substitutes the acyl (RCO-) group into a molecule, generally for an active hydrogen.

acyloin condensation The formation of an acyloin, very often cyclic by condensing two molecules of ester with sodium.

acyloins 1,2-Ketoalcohols of the type R-CO-CHR'-OH. See acetoin, benzoin.

adamantane, C<sub>10</sub>H<sub>16</sub>. Colourless hydrocarbon,



m.p. 269°C, but subliming readily at room temperature and atmospheric pressure. Occurs (up to 0.0004%) in some petroleum fractions, together with alkylated adamantanes. Has a rigid ring system composed of three fused chain cyclohexane rings, having the same configuration as the diamond lattice. Synthesized by a Lewis-acid catalysed rearrangement of tetrahydrodicyclopentadiene. 1-Substituted derivatives are available by direct substitution, e.g. by Br2. 1-Adamantanamine hydrochloride has been found useful in viral infections, where it acts by preventing penetration of the host cell by the viral particle; it also finds application in treating Parkinson's disease. Adamantyl derivatives are used as lubricants and resins.

Adams' catalyst, platinum oxide, PtO<sub>2</sub>·H<sub>2</sub>O. Produced by fusion of H<sub>2</sub>PtCl<sub>6</sub> with sodium nitrate at 500-550°C and leaching of the cooled melt with water. The brown oxide is stable in air but is activated by exposure to hydrogen. Used as a hydrogenation catalyst for converting alkenes to alkanes at ambient pressure and temperature. Nitro groups can be converted to amino groups but carbonyl groups are usually unaffected. Modifications improving activity include deposition on silicic acid.

adatom An adsorbed atom.

addition reactions Reactions in which an unsaturated system (C=C, C=C, C=O, etc.) is saturated or part saturated by addition of a molecule across the multiple bond. Examples include the reaction of bromine with ethene to give 1,2-dibromoethane, hydrogen cyanide addition to an aldehyde giving a cyanhydrin, the Diels-Alder reaction, and addition polymerization. Also used in inorganic chemistry, e.g. the reaction of BF<sub>3</sub> with nucleophiles, e.g. ammonia, ether, and various reactions of complexes where the co-ordination number of the metal atom is effectively increased.

additives The general term used to describe compounds, usually added in small amounts, which will confer specific properties on the bulk material, e.g. anti-foaming additives for lubricating oils.

additive volumes, law of The volume occupied by a mixture of gases is equal to the sum of the volumes which would by occupied by the constituents under the same conditions of temperature and pressure.

**adduct** A phase (often a compound) formed by direct combination, generally in simple proportions, of two or more different compounds or elements.

adenase The enzyme deaminating adenine to hypoxanthine, but not of wide distribution. Guanase however, is found widely distributed in liver, kidney, spleen, etc.

adenine, 6-aminopurine, C<sub>5</sub>H<sub>5</sub>N<sub>5</sub>. Crystallizes

with 3H<sub>2</sub>O which it loses at 110°C. Sublimes at 220°C, m.p. 360-365°C (decomp.). Almost insoluble in cold water, but more soluble in hot. Sparingly soluble in alcohol. Adenine is a constituent of the nucleic acid portion of nucleoproteins, and, combined, as adenosine pyrophosphate; it plays an important part in many metabolic processes

adenosine See nucleosides.

adenosine diphosphate (ADP) ADP is adenosine 5'-diphosphate (pyrophosphate). It is a precursor of ATP and is also formed from it during processes in which ATP is involved.

adenosine monophosphate (AMP) Normally refers to adenosine 5'-phosphate (muscle adenylic acid), an important structural component of nucleic acids \* and of several coenzymes, e.g. nicotinamide adenine dinucleotide (NAD), flavin adenine dinucleotide (FAD) and coenzyme A. Adenosine 2'-phosphate (adenylic acid a) and 3'-phosphate (adenylic acid b) also occur in nucleic acid hydrolysates. Further phosphorylation of adenosine 5'-phosphate affords the 5'-pyrophosphate (adenosine diphosphate, ADP) and 5'-triphosphate (adenosine triphosphate, ATP\*). See also cyclic AMP

adenosine triphosphate (ATP) ATP is the most

important of the so-called 'high-energy compounds', a group of naturally-occurring organic phosphates characterized by high free energies of hydrolysis, and playing a fundamental role in biosynthesis and active transport and muscle action. Phosphorylation of ADP to yield ATP occurs (1) during photosynthesis, (2) during fermentation, (3) during respiration (see oxidative phosphorylation). ATP is the primary source of energy in the metabolism of plant, animal and

bacterial cells. Energy may be conveyed to other molecules (a) through transfer of the AMP moiety with concomitant release of pyrophosphate; enzymic hydrolysis of the latter to phosphate prevents the reversal of the transfer; (b) through transfer of the terminal phosphate group and release of ADP.

adenylic acid See adenosine monophosphate.

adhesion agents Any additive which will improve the adhesivity of a material. The term generally applies to surface-active agents used to prevent stripping of an adhesive from a surface by water. They are widely used in road bitumens, particularly cutback bitumens\*, used in surface dressings and in coated macadam surfacings.

Soaps of heavy metals have been used but cationic surface-active agents have proved more suitable, notably organic amines of relatively high molecular weight. The use of quaternary ammonium compounds, although advocated, has not proved reliable in road surfacings.

**adhesive** A material which will wet two surfaces which are to be joined and which will subsequently solidify to form a join.

adhesives Materials used to bond solids together. Examples include glues (starches, proteins), thermoplastic resins, thermosetting resins, rubber, asphalt, sodium silicates.

adiabatic change A change in which heat is neither allowed to escape from, nor is added to, the system during the change.

adipic acid, C<sub>0</sub>H<sub>10</sub>O<sub>4</sub>, HOOC·[CH<sub>2</sub>]<sub>4</sub>·COOH. Colourless plates; m.p. 153°C. Slightly soluble in water, soluble in alcohol and ether. Present in beet-juice; manufactured by the air or nitric acid oxidation of cyclohexanol, the latter being obtained by the air oxidation of cyclohexane. Distillation of its calcium salt gives cyclopentanone. It forms long chain polymers with diamines and is very largely used in the manufacture of nylon. It is also used for the manufacture of plasticizers and certain vinyl and urethane plastics. U.S. production 1978 770 000 tonnes.

adlayer An adsorbed layer.

Admiralty brass See brass.

ADP See adenosine diphosphate.

adrenaline, epinephrine, C<sub>9</sub>H<sub>13</sub>NO<sub>3</sub>. M.p. 212°C.

Insoluble in water and most organic solvents, soluble in mineral acids. It is secreted along with noradrenaline\* by the adrenal medulla, from which it may be obtained. Alternatively it may be synthesized by treating catechol with chloroacetyl chloride, treating the product with methylamine, reducing, and resolving with (+)-tartaric acid.

Intravenous injection causes a rise in blood pres-

sure by increasing the heart rate and stroke volume, and by constricting the small arteries in most tissues; arteries in skeletal muscle and the heart, on the other hand, are dilated by adrenaline. It inhibits peristaltic movements of the gut, liberates glucose from the liver and dilates the bronchi. It is used as the acid tartrate in the treatment of allergic reactions and circulatory collapse. It is included in some local anaesthetic injections in order to constrict blood vessels locally and slow the disappearance of anaesthetic from the site of injection. Ultimately it induces cellular activation of phosphorylase which promotes catabolism of glycogen to glucose.

adrenocorticotropic hormone, ACTH, corticotropin A polypeptide hormone, of 39 amino-acid residues secreted by the anterior lobe of the pituitary gland. It is obtained commercially from the glands of cattle, sheep and pigs. ACTH stimulates the adrenal cortex, promoting the metabolism of cholesterol to corticosteroid hormones: the concentration of these in the circulating blood is one of several factors influencing the production of ACTH. ACTH is used to detect adrenal deficiency, as a patient with nonfunctioning adrenals will not respond with a rapid increase in hydrocortisone level.

adsorbate The substance which is adsorbed onto the surface of the adsorbent.

adsorbent The substance upon whose surface the process of adsorption occurs.

adsorption Because of the abnormal condition of the atoms at the surface of a solid or a liquid compared with atoms in the bulk, the surface of a solid or liquid is a seat of free energy. The process of adsorption in which foreign atoms or molecules become attached to the surface lowers the free energy of the surface. Thus, e.g., adsorption of detergent molecules at liquid surfaces lowers the surface tension of the liquid.

Adsorption may in principle occur at all surfaces; its magnitude is particularly noticeable when porous solids, which have a high surface area, such as silica gel or charcoal are contacted with gases or liquids. Adsorption processes may involve either simple unimolecular adsorbate layers or multilayers; the forces which bind the adsorbate to the surface may be physical or chemical in nature.

Adsorption is of technical importance in processes such as the purification of materials, drying of gases, control of factory effluents, production of high vacua, etc. Adsorption phenomena are the basis of heterogeneous catalysis and colloidal and emulsification behaviour.

adsorption, chemical See chemisorption.

**adsorption column chromatography** See chromatography.

**adsorption indicator** An indicator which functions by adsorption on the surface of a precipitate.

Thus in precipitating AgCl in the presence of excess Cl<sup>-</sup> the surface has a layer of Cl<sup>-</sup> and is negatively charged; in the presence of the indicator fluorescein the indicator is in solution. As soon as there is excess of Ag<sup>+</sup> the precipitate takes on a positive charge and the presence of the fluorescein anion as counter ion gives the precipitate a pink-ish-red colour.

adsorption, industrial Adsorption is of considerable industrial importance, being employed, for example, in the refining of lubricating oils, the decolourizing of sugar solutions and the purifying and drying of gases. Industrial adsorption may employ one of three principle methods. In batch operations the adsorbent and liquid are contacted, with subsequent separation by filtration or settling. In fixed bed operations the liquid or gas is passed through a bed of adsorbent which may be periodically regenerated. In continuous countercurrent operations the adsorbent and fluid flow countercurrent to each other, the adsorbent being continuously regenerated in another part of the system. See also adsorption and adsorption, physical.

adsorption, physical Many adsorption processes are not chemically specific and are readily reversible. The forces of attraction between the adsorbate and adsorbent are weak and similar in nature to those responsible for the cohesion of molecules in the liquid state, namely, van der Waal's forces\*. For this reason physical adsorption often involves the formation of multiple layers at the adsorbent surface.

aerosol, aerogel A dispersion in which a finely divided solid is suspended in a gas is common, and is exemplified by smoke. When the dispersion medium is air and the particles are of colloidal dimensions, the system is termed an aerosol. Aerosols can often be formed by the rapid condensation of a vapour such as that of a metal oxide. Nickel aerosols have been made by vaporization of the metal in an arc or by heating nickel carbonyl vapour. By condensation of such sols, nickel aerogels are formed.

Cosmic dust and the stable dust sometimes formed by volcanic eruption are naturally occurring aerogels.

Aerosol sprays consist of a material dissolved or suspended in a liquid which when pressure is released volatilizes to produce a fine spray. The spray carries the active material. Used in hair lacquers, paints, etc.; the propellant should be inert and non-inflammable. Chlorofluorocarbons have been used extensively but are now being replaced.

Aerosol is also a trade name for certain wetting agents, most of which are esters of sodium sulphosuccinic acid. Aerosol OT Dry is the dioctyl ester and is a very powerful wetting agent.

aesculin, C<sub>15</sub>H<sub>16</sub>O<sub>0</sub>. A coumarin glycoside \*, m.p. 205°C. It has glucose attached at position 6 to 6,7-dihydroxycoumarin. It is found in horse-chestnut bark and leaves.

aetiophyllin See chlorophyll.

aetioporphyrin See porphyrins.

affinity, chemical The chemical affinity of one substance for another is a measure of the tendency of the two substances to enter into chemical combination. The concept of affinity dates from the early days of chemistry. The term 'affinity of a chemical reaction' is used to denote the change of free energy in the system when the reaction takes place; this is a true measure of the tendency to react.

affinity chromatography A method of purifying natural macromolecules, especially proteins, which is of increasing importance in biochemistry. It depends on covalently attaching a specific ligand to an insoluble inert support. The ligand must have a special and unique affinity for the macromolecule, so that on passage in solution down a column of the material the macromolecule is preferentially retarded and thus separated from contaminating molecules. An example of a ligand type is the substrate or substrate-analogue of an enzyme (though preferably not being irreversibly changed during the operation).

aflatoxins The toxic metabolites of the fungus

Aspergillus flavus Link ex Fries. The fungus is found in grain crops and peanuts and the aflatoxins are extremely toxic and carcinogenic. Four aflatoxin isomers  $[B_1, B_2, G_1]$  and  $[G_2]$  of the structure shown are known.

Ag Silver.

agar, agar-agar A seaweed colloid\*. A mixture

of two polysaccharides, agarose and agaropectin. Agarose, the main constituent, is a well-defined neutral polysaccharide containing 3,6-anhydro-L-galactose and D-galactose as the repetitive unit. Agaropectin contains the carboxyl and sulphate groups of native agar.

Agar occurs as a cell-wall constituent of the red marine algae *Rhodophyceae*, from which it is extracted by hot water, and marketed as a dry powder, flakes, or strips. It dissolves in hot water and sets on cooling to a jelly at a concentration as low as 0.5%. Its chief uses are as a solid medium for cultivating micro-organisms, as a thickener,