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THE PENGUIN

# DICTIONARY OF CHEMISTRY

D. W. A. SHARP



#### PENGUIN REFERENCE BOOKS

# THE PENGUIN DICTIONARY OF CHEMISTRY

David William Arthur Sharp was born in 1931 and educated at Ashford Grammar School, Harvey Grammar School, Folkestone, and Sidney Sussex College, Cambridge. From 1957 until 1961 he was a lecturer at the Imperial College of Science and Technology, London, and between 1965 and 1967 he was Professor of Chemistry at the University of Strathclyde, Glasgow. Since 1968 he has been Professor of Chemistry at the University of Glasgow. He was a contributor to the third, fourth and fifth editions of Miall's Dictionary and editor of the fifth edition. He has written many papers for learned journals in his field.

# THE PENGUIN DICTIONARY OF CHEMISTRY

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# Preface

In this Dictionary I have aimed to provide an explanation of the terms used in the various branches of chemistry, together with brief accounts of important substances and chemical operations. The Dictionary is intended for use in schools, colleges and universities from the first study of chemistry up to about second year at university or college. We have necessarily had to be selective rather than comprehensive but most chemicals met with at this level should be included.

We have paid particular attention to industrial processes and have tried to give some 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. (World, U.S. or European production figures are used as seem most appropriate or up-to-date – and it must be remembered that for many speciality chemicals U.S. production is dominant.)

The nomenclature used is that which we consider to be the most likely to be met in context by users of the Dictionary. Thus, for simple compounds systematic nomenclature is used, but for more complex species the most common name is used. Cross-references are used wherever possible.

The list of contributors is on page 6 and I am deeply indebted to them, for it is they who originally prepared *Miall's Dictionary of Chemistry* from which this Dictionary has been compiled. 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:

```
Å
                     Ångström unit, 10<sup>-8</sup> cm
Ar
                     aromatic group
                     atomic number
at no.
                     atomic weight
at.wt.
b.p.
                     boiling point
Bu
                     butyl group
                     see optical activity, chirality
D-, DL-
E
                     energy
Et
                     ethyl group
G
                     Gibbs function (see free energy)
g
h
                     Planck's constant
H
                     enthalpy
L-
                     see optical activity, chirality
L
                     Avogadro's number
lbs.
                     pounds
                     mega (106) million
m
M
                     molar
M (in formulae)
                     any metal
Me
                     methyl group
                     millilitre '
ml
mol.wt.
                     molecular weight
                     melting point
m.p.
Nm
                     nanometres
0
                     ortho
                     per annum
p.a.
                     para
D
Ph
                     Phenyl group
                     see hydrogen ion concentration
pH
R
                     alkyl group
R
                     gas constant
                     see optical activity, chirality
R
S
S
                     see optical activity, chirality
X (in formulae)
                     any non-metal (usually a halogen)
                     micron
μ
                     frequency
                     see optical activity, chirality
(+)- and (-)-
```

For simple compounds the main reference uses the systematic I.U.P.A.C. nomenclature, and other nomenclature is cross-referenced to the systematic name.

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

AAS Atomic absorption spectroscopy\*.

abherents, release agents, parting agents
Liquid or solid films which reduce or prevent
adhesion between surfaces; solid-solid, solidpaste, 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, C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>. A crystalline diterpenoid carboxylic acid m.p. 172–175°C, obtained from pine rosin by acid treatment. 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 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.

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 lique-faction or solidification. The absolute zero  $(0\,\mathrm{K})$  is  $-273\cdot16^\circ\mathrm{C}$  i.e.  $\frac{1}{213\cdot16}$  of the triple point of water, and one degree absolute is equivalent to one degree Celsius or Centigrade.

$$T(K) = temperature (^{\circ}C) + 273.16$$
.

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 consisting of a column or tower, usually circular in cross-section, the absorbing liquid passing down counter-current • to the gas passing upwards.

When the main object of the absorption is to remove impurities these columns are often referred to as scrubbers\*.

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.

absorption tower See absorption column.

ABS plastics A group of plastic materials based on blended copolymers of styrene-acrylo-

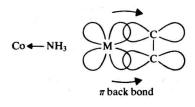
nttrile (70:30) and butadiene-acrylonitrile (65:35) and on graft interpolymers of styrene and acrylonitrile with polybutadiene. Used in pipe (25%), appliances (20%), and automotive parts (15%). U.S. consumption 1979 530 000 tonnes.

Ac Actinium. Also used for ethanoate (acetate).

acac Abbreviation for acetylacetonato group.

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, e.g. diphenyl-guanidine\*, the thiazoles, e.g. mercaptobenz-thiazole\*, and the thiuram disulphides\*. The term is also used for those substances which act as catalysts by increasing the rate at which thermosetting resins cure or harden.

acceptor An atom, molecule, or ion that is electron deficient and which can form a coordinate link \* with an electron donor. Thus in the complex ion  $[Co(NH_3)_0]^{3+}$  the coball(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, e.g. metal-olefine complexes.



Also 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.

accumulator See lead accumulator.

acenaphthene, C<sub>12</sub>H<sub>10</sub>. Colourless needles, m.p. 95°C, b.p. 278°C. It is important as a

dyestuff intermediate, being used as a source of nitro- and amino-derivatives.

acenaphthenequinone, C<sub>12</sub>H<sub>0</sub>O<sub>2</sub>. Yellow needles, m.p. 261 C. It is condensed with thioindoxyl and its derivatives to bright scarlet and red vat dyes.

acenaphthylene, C<sub>12</sub>H<sub>8</sub>. Yellow plates, m.p. 92 93 C (decomp.). It is derived from acenaphthene by catalytic dehydrogenation (1, 2) and polymerizes to give plastic products.

acetal,  $C_0H_{14}O_2$ ,  $CH_3$ - $CH(OEt)_2$ . A pleasant-smelling liquid, b.p. 104-105 C. Prepared by mixing ethanal and ethanol in the presence of a catalyst, such as HCl, or by passing  $C_2H_2$  into EtOH in the presence of a catalyst.

acetaldehyde See ethanal.

acetal resin See aldehyde polymers.

acetals Compounds of the general formula:

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. Some acetals are useful solvents.

acetamide See ethanamide.

acetanilide, C<sub>8</sub>H<sub>0</sub>NO, PhNH-CO-CH<sub>3</sub>.

White crystals, m.p. 114°C. Manufactured by reacting aniline with excess ethanoic acid or ethanoic anhydride. Chief use is in the manufacture of dye intermediates such as *p*-nitroactanilide, *p*-nitroaniline and *p*-phenylene-diamine, 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 plastics.

acetates Salts or esters of ethanoic acid\*.

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 monotwo di-, and one tri-acetate. The commercial acetins are mixtures of the various acetates and form colourless or slightly brown syrupy

liquids. Prepared from glycerol, ethanoic acid and sulphuric acid.

Monoacetin contains chiefly the 1-acetate CH,OH-CHOH-CH,OOCCH1. Used as a solvent for the dyes employed in printing paper

Diacetin is chiefly the 1:3-diacetate CH2OOCCH3+CHOH+CH2OOCCH3. Used as plasticizer for cellulose acetate lacquers and as a solvent for basic dyes.

Triacetin is about 90% glycerol triacetate and 10% diacetate. Used as a plasticizer for lacquers and as a solvent for gums and resins.

# acetoacetic acid, acetonemonocarboxylic acid, butan-3-onoic acid, C4H6O3,

CH<sub>3</sub>CO-CH<sub>2</sub>COOH. A colourless 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.

acetoacetic ester See ethyl acetoacetate.

3-hydroxy-2-butanone, CAHRO, CH3CH(OH)COCH3. M.p. 15°C, b.p. 148°C. Produced from propene and butene glycols by the action of ethanoic acid bacteria, and from ethanal by yeast and 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, C5H6O5, CO-(CH2COOH)2. Colourless needles, m.p. 135°C (decomp.). Prepared by the action of sulphuric acid on citric acid. Readily decomposed by boiling water, acids, or alkalis to acetone (propanone) and carbon dioxide. 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,CN. Poisonous liquid. b.p. 82°C. 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>3</sub>-.

acetonylacetone See hexan-2.5-dione.

acetophenone, C<sub>8</sub>H<sub>8</sub>O, PhCOCH<sub>3</sub>. Colourless plates, m.p. 20°C. Odour resembling bitter almonds. Prepared by the action of ethanoyl chloride upon benzene in the presence of aluminium chloride. Typical ketone. Oxidized by potassium permanganate to phenylglyoxylic acid. Used as a solvent for cellulose ethers.

acetoxy The group CH, COO-.

acetylacetonates Metal derivatives of acetyl-

acetone generally containing the grouping shown (Macac) with some delocalization in the ring. The number of acetylacetonate groups bonded to the metal can vary from 1 to 4.

acetylacetone, C5H8O2, CH3COCH2COCH3. A diketone with enolic properties. The enolate ion acac forms stable complexes with many metals, e.g. tris(acetylacetonato)iron(III), Feacac3. Metal derivatives are generally soluble in organic solvents and often appreciably volatile; they are used in solvent extraction and mass spectrometry.

Derivatives of acetylacetone, CF3COCH2COCH3, CF3COCH2COCF3 and thienyl-COCH, COCF, form particularly stable derivatives.

acetylation, ethanoylation A process for introducing acetyl groups into an organic compound containing OH, NH, 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, C2H12NO3, (CH<sub>3</sub>)<sub>3</sub>N+CH<sub>2</sub>CH<sub>2</sub>OOCCH<sub>3</sub>OH A zwitterion. Passage of a nerve impulse from a nerve end to another nerve or muscle cell causes release of acetylcholine to transmit hempulse across the intercellular space. The acetylcholine is quickly destroyed by the hydrolytic action of acetylcholine esterase. Injection of acetylcholine can cause dilatation of the arteries.

acetyl coenzyme A A reactive thioester of fundamental importance in metabolism and biosynthesis. 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 olefine complexes\*.

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

acetylene dichloride See dichloroethenes.

acetylene tetrachloride See sym-tetrachloroethane.

acetylides Carbides\* containing  $C_2^{2-}$  or  $C_2R^-$  species. Formed by more electropositive elements (e.g. K, Ca, Al) and by some transition elements (e.g. Cu, Ag, Au). Hydrolysed to ethyne. Many transition metal acetylides are explosive.

Also metal derivatives of terminal alkynes, RC<sub>2</sub>H. Transition metals form complex acetyldes (e.g.  $[M(C \equiv CR)_n]^{k-1}$ ) often containing the metal in low oxidation states.

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 do not exist except in the gas phase, 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,  $H_1O^+$ .

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

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

and ionic amides are bases in 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 in that system. Thus bromine trifluoride ionizes

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 AICl<sub>3</sub> can accept a pair of electrons from a chloride ion forming the [AICl<sub>4</sub>]<sup>-</sup> ion and is a Lewis acid.

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 chromophoric 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>7</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 alkali extract of phenol derivatives formed in the production of gasoline by cracking operations. Also referred to as cresylic acids \* or 'phenols'.

acid rain Rain containing acidic impurities (SO<sub>2</sub>, nitrogen oxides) generally from industrial pollution.

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 and used for the metal processing, textile and leather industries.

aconitic acid,  $C_0H_0O_0$ . Unsaturated acid prepared by dehydrating citric acid with 50% sulphuric acid.

aconitine, C<sub>34</sub>H<sub>47</sub>NO<sub>11</sub>. Intensely poisonous alkaloid obtained from *Aconitum napellus*, monksbane, m.p. 197°C.

acridine, C<sub>13</sub>H<sub>9</sub>N. Colourless needles, m.p. 111°C.

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

acrolein See propenal.

acrolein polymers, propenal polymers Polymers of CH<sub>2</sub> = 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.

acrylate resins and plastics Generally used to refer to polymeric methyl acrylate (methyl propenoate) and polymeric methyl methyl acrylate (methacrylate) (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 1986 279 000 tonnes.

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 flocculating agents, in paper making, and if co-polymerized with e.g. divinylbenzene as ion-exchange resins.

acrylonitrile See propenenitrile.

acrylonitrile polymers See polyacrylonitrile.

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 oxidation states 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  $^{227}$ Ac is very radioactive ( $t_1$  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

activated adsorption Chemisorption often has an activation energy associated with it and is sometimes referred to as activated adsorption.

activated carbon See active carbon.

activated clay See bleaching earths.

activated molecule 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 may be activated by light or by heat. Molecules will only react on collision when they possess more than a certain minimum amount of energy.

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  $(E_{\rm a})$  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>. Used as an adsorbent for removal of small traces of impurities from a gas or liquid. 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. See carbon black.

active centres In heterogeneous catalysis adsorption is considered to occur at active centres on the surface of the catalyst. Active centres are the specific sites at which adsorption occurs. The concept of active centres has been extended to enzymes and bacterial action.

active earths See bleaching earths.

active mass The thermodynamic activity\*.

An old terminology.

active transport The biochemical transport of substances, usually against a concentration gradient, other than by osmosis or diffusion.

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  $\bullet$  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  $\bullet$ . 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 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. Normally a more active element higher in the series will displace a lower element from its compounds.

actomyosin The most important protein of muscle.

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. ethanoyl chloride, CH<sub>3</sub>CO-Cl, is the acyl chloride formed from ethanoic acid, CH<sub>3</sub>CO-OH. 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 of e.g. an -OH group.

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, C10H10. Colourless hydro-



carbon, 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 from tetrahydrodicyclopentadiene. 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, PtO2nH2O. Produced by fusion of H, PtCl, with sodium nitrate at 500-550°C and leaching of the cooled melt with water. Stable in air, activated by hydrogen. Used as a hydrogenation catalyst for converting alkenes to alkanes at low pressure and temperature. Often used on SiO2.

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 BF3 with nucleophiles, e.g. ammonia, ether, to form complexes where the co-ordination number or the oxidation state of the metal atom is increased.

additives 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 be 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.

## adenine, 6-aminopurine, C,H,N,.

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) Adenosine 5'diphosphate (pyrophosphate). A precursor of ATP and is also formed from it during processes in which ATP is involved.

adenosine monophosphate (AMP) Normally adenosine 5'-phosphate (muscle adenylic acid), an important structural component of nucleic acids\* and of several coenzymes. See also cyclic AMP.

adenosine triphosphate (ATP) 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. ATP is the primary source of energy in the metabolism of plant, animal and bacterial cells.

adenylic acid See adenosine monophosphate. adhesion agents Any additive which will improve the adhesivity of a material. Surfaceactive 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.

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. Used in construction, packaging, textiles, furniture, and electrical goods.

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>e</sub>H<sub>10</sub>O<sub>4</sub>, HOOC·[CH<sub>2]4</sub>·COOH. M.p. 153°C. Present in beet-juice; manufactured by the air or nitric acid oxidation of cyclohexanol. 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 1986 690 000 tonnes.

adlayer An adsorbed layer.

ADP See adenosine diphosphate.

adrenaline, epinephrine, CoH13NO3. M.p.

212°C. It is secreted along with noradrenaline\* by the adrenal medulla, from which it may be obtained. It may be synthesized from catechol. 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.

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 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 pinkish-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 batch, fixed bed, or continuous countercurrent operations.

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, van der Waals' forces\*. 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 air and the particles are of colloidal dimensions, e.g.