Concise Encyclopedia Chemistry

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Translated and revised by
Mary Eagleson

Walter de Gruyter Berlin · New York 1994

Title of the original, German language edition
ABC Chemie

Edited by
Dr. Hans-Dieter Jakubke and Dr. Hans Jeschkeit

Bibliographisches Institut & F. A. Brockhaus AG
D-68003 Mannheim

Translated into English and revised by
Mary Eagleson, Ph. D.

♾ Printed on acid-free paper, which falls within the guidelines of the ANSI to ensure permanence and durability.

Library of Congress Cataloging-in-Publication Data

ABC Chemie. English.
Concise encyclopedia chemistry / translated and revised by Mary Eagleson.
ISBN 0-89925-457-8
1. Chemistry–Encyclopedias. I. Eagleson. Mary, 1945–
II. Title.
QD4.A2313 1994
540'.3–dc20

Die Deutsche Bibliothek – CIP-Einheitsaufnahme

Concise encyclopedia chemistry / transl. and rev. by Mary Eagleson. – Berlin ; New York : de Gruyter, 1994
Dt. Ausg. u. d. T.: Fachlexikon ABC Chemie
ISBN 3-11-011451-8
NE: Eagleson, Mary [Übers.]

English language edition

Typesetting and Printing: Buch- und Offsetdruckerei Wagner GmbH, Nördlingen.
Binding: Lüderitz und Bauer, Berlin.
Cover Design: Hansbernd Lindemann, Berlin.

From the preface of the original edition

This **Concise Encyclopedia of Chemistry** offers an informative overall view of the wide field of chemistry in a handy, compact volume.

Care has been taken to combine scientific precision with a clear presentation so that this handbook is not just a useful reference tool for chemists and laboratory technicians but also for lecturers, teachers and students of chemistry, biochemistry, pharmacy, biology or medicine.

The publishers and editors were presented with the difficult task of processing the vast increase of knowledge accumulated over the past twenty years and presenting it within the tried and tested framework of an alphabetical encyclopedia. It was at this point that the limits imposed on the volume of the book became clear.

Aspects of other related fields were kept to a minimum; please note that an encyclopedia of biochemistry has also been published*. A certain shift in emphasis can be seen towards the chemical substances and their structural formulas. However, apart from the chemical elements, their reactions and compounds, the most important natural substances, synthetics, pharmaceuticals, dyes etc. have been included, as well as the complex atomic and molecular structure of matter, stoichiometry, analysis, catalysis, chemical kinetic reactions and thermodynamics, electrochemistry, colloid chemistry, carbon chemistry and petrochemistry, etc.

An encyclopedia cannot – and should not – take the place of a textbook; rather, should give a concentrated overview of chemistry, such as a handbook does. However, a book such as this can provide a mine of information for the reader, who uses it not just as a reference work to be consulted in cases of sudden need, but will also often just browse through its pages.

The **Concise Encyclopedia of Chemistry** contains around 12,000 entries taken from the fields of general, inorganic, organic, physical and technical chemistry, complemented by some 1,600 figures and 300 tables. References have not been given due to the problem of the relatively long life of such encyclopedic works.

The internationally valid nomenclature has been used and a detailed entry "Nomenclature" informs the reader of the IUPAC regulations for the naming of chemical elements and compounds. The book contains a periodic table, together with tables of the elements, SI units and physical constants.

The publishers and editors are aware that, in spite of their efforts, it is impossible to include all aspects of chemistry in one manageable volume. Some readers may feel that the choice of entries, the weighting of the different fields of chemistry, and the method and depth of presentation are not always the best. Specialists in the various chemical disciplines may think that their particular area has not received its due attention. Everyone involved, scientists in research, teaching or industry, has done their utmost to ensure that this encyclopedia is of a high standard. Therefore, the publishers, editors and authors alike welcome your suggestions for the revision of any ensuing editions.

* **Concise Encyclopedia Biochemistry**, Second Edition.
Revised and expanded by Thomas Scott and Mary Eagleson.
1988. 650 pages. Hardcover. ISBN 3-11-011625-1
Published by Walter de Gruyter, Berlin · New York

How to use this book

Throughout this book, the chemical elements and compounds have been namend mainly according to the recommended rules of the IUPAC (International Union for Pure and Applied Chemistry).

Entries are listed in alphabetical order. Numbers, Greek letters and configurational numbers/ letters at the beginning of names are ignored in the allocations of alphabetical order, e.g. 2-Nitro-benzaldehyde is listed under N; α-Oximino ketones is listed under O.

Standard abbreviations, e.g. NMR, DNA, EDTA etc., are found as entries in the appropriate alphabetical positions. If the main entry title is repeated in the text, then the entry title is abbreviated to its first letter, e.g. "**Heme:** an iron (II) complex of a porphyrin. H. are found in nature". An exception to this rule can be observed under the entries of the elements where the entry title is either abbreviated to its first letter or its chemical symbol is given, e.g. **"Cadmium**, symbol *Cd* ... Properties: Cd is a silvery white, relatively soft metal". Other abbreviations – when not explained in the text – are listed below.

Cross referencing is indicated by the word "see" and the subject of the cross reference starts with a capital letter, e.g. "... is transported mainly in Pipelines (see) ...", or "... see Nickel sulfate".

The main entry title is printed in bold type, followed by synonyms in bold italics. Any further relevant terms within the text are stressed by means of italics.

Physical quantities are given in SI-units.

Some of the figures and formulas were taken directly from the original German book. Therefore, it is possible that, in some cases, the German abbreviations still remain in the figures e.g. AS = AA, DNS = DNA, Peptid = peptide.

Other abbreviations:

abb.	abbreviation
[α]	specific optical rotation
b.p.	boiling point
c	concentration
°C	degrees Celsius
crit.	critical
(d.)	with decomposition
d	density
IP	isoelectric point
M	molar mass
M	molar
m.p.	melting point
M_r	relative molecular mass
n	refractive index
syn.	synonym
T	temperature
V	volume
Z	atomic number

A

a: symbol for axial bonds; see Sterioisomerism, 2.2.

A: 1) formula symbol for absolute atomic mass. 2) *A*, symbol for activity of a radioactive substance. 3) A_E, see Electrophilic reactions. 4) A_N, see Nucleophilic reactions. 5) A_r, symbol for relative atomic mass. 6) A_R, see Radical reactions.

α: configuration symbol. In organic nomenclature, it denotes a substituent on the carbon adjacent to a principal group; for example,

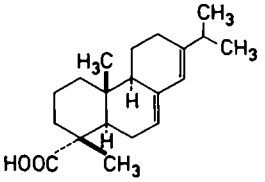
CH_3–CH(–NH_2)–COOH

is α-aminopropanoic acid. In inorganic nomenclature, α is used to designate one of the modifications of a polymorphic element or compound (see Polymorphism).

AAS: abb. for Atomic absorption spectroscopy (see).

Abadol: same as 2-Aminothiazol (see).

Abietic acid: abieta-7,14-diene-19-carboxylic acid, a tricyclic diterpene acid; colorless crystals, m.p. 173 °C. It is practically insoluble in water, but soluble in alcohol and ether. The esters and salts are called abietates. A. is a resin acid, and the main component of conifer resins. Colophony consists of about 43% A. It is used industrially in the preparation of paints, soaps, varnishes and plastics.



Abrasives: very hard materials used in sanding and polishing. The grains of the abrasive may either be fixed (as on sandpaper) or free. The main characteristics of A. are hardness and grain size. Both natural and synthetic A. are used.

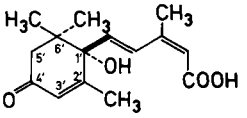
1) ***Natural A.*** are hard minerals which are granulated and sorted by sieving. a) *Diamond* is the hardest naturally occuring mineral, with a Mohs hardness of 10. The larger crystals are used as grinding diamonds for preparation of other A. The small to fine grains are used for grinding disks and abrasive pastes for grinding the hardest substances, for example rubies for clock works, sintered corundum, sintered metals, etc. b) *Corundum* is chemically aluminum oxide, α-Al_2O_3. Its Mohs hardness is 9. c) *Emery* is a mixture of corundum, magnesite, specular iron and quartz. Because of their limited occurrence, corundum and emery are of limited significance.

2) ***Synthetic A.*** are produced in various ways (see Crystal growing). a) Synthetic *corundums* are used; their hardness depends on their content of Al_2O_3. Grindstones are made with normal corundum, containing 95 to 97% Al_2O_3 (medium hard), or white or pink fine corundum which contains about 99% Al_2O_3 (hard). Ruby corundum, consisting of Al_2O_3-Cr_2O_3 mixed crystals with up to 3% Cr_2O_3, is used mainly for fine grinding. b) *Silicon carbide*, α-SiC, has a Mohs hardness of 9.5. c) Synthetic *diamonds* are harder than natural diamonds. d) *Boron nitride*, (regular) BN, is as hard as synthetic diamonds.

Solid ***grindstones*** consist of the A. grains and bonding phases consisting of hard (epoxide or phenol formaldehyde) and elastic resins, together with ceramic binding masses (mixtures of clay, feldspar, quartz and kaolin). A metallic binding matrix (Fe, Ti, V, Nb, Mo or W) is preferred for high-performance grindstones with diamond A. The properties of a grindstone depend on the nature of the binding matrix as well as on the type of A. and its grain size. Corundum disks are most commonly used for steels, while silicon carbide disks are used for chilled castings, aluminum, brass, copper and cast iron. Diamond stones are used for hard metals, glass, ceramics, concrete, stone and nonferrous metal alloys.

ABS: abb. for Alkylbenzene sulfonates (see).

Abscisic acid, obsolete name, ***dormin***: (S)-5-(1-hydroxy-2,6,6-trimethyl-4-oxo-1-cyclohexenyl)-3-methyl-*cis,trans*-penta-2,4-dienoic acid, a phytohormone; chemically, a monocyclic sesquiterpene. A. forms colorless crystals, m.p. 160-161 °C, which are readily soluble in organic solvents, but poorly soluble in water. It is very sensitive to light, which causes a rearrangement to the inactive *trans, trans*-isomer. A. suppresses the effects of other phytohormones, and thus is a natural growth inhibitor. Together with the growth-promoting phytohormones, e.g. the cytokinins, A. regulates ageing processes, shedding of leaves, formation of blossoms, fruit ripening and other important development processes in the plant.



Absorbance: same as Extinction (see).

Absorbate: the gas taken up by absorption.

Absorbent: a condensed phase which takes up the absorbate in the process of absorption.

Absorbt: the molecularly dispersed substance in the absorbent after absorption.

Absorptiometry: a term which encompasses Photometry (see) and Colorimetry (see).

Absorption:

1) A. of gases: uptake of a gas into the interior of a condensed phase in a molecular-disperse distribution. In reversible, physical A., the equilibrium partial pressure of the absorbate over the solution is significant, and depends on the concentration of gas already dissolved in the liquid. Complete uptake of the absorbate by the absorbent is not possible. However, if a chemical reaction occurs and the vapor pressure of the absorbed substance over the solution is low, a complete A. is theoretically possible. If the compound formed by the reaction is unstable, an equilibrium pressure of the absorbate over the solution will develop.

Henry's Law, which is analogous to the Nernst distribution, applies to ***physical A.***: at constant temperature, the saturation concentration c of a gas in a solution is proportional to the partial pressure p: $c = \alpha p = n/v$. In this formula, v is the volume of the liquid, c is the saturation concentration of the gas in the solution, n is the number of moles of the dissolved gas, and α is Bunsen's absorption coefficient.

In the A. of a mixture of gases, an equilibrium is established for each component which corresponds to its partial pressure and solubility coefficient. ***Exsorption*** is the loss of an absorbed gas by increase in temperature, decrease of pressure on the solution, or treatment with an inert gas. After *chemical A.*, exsorption is possible only if the compound formed by the reaction is unstable and a certain partial pressure of the absorbed gas can be established over the liquid.

A. is used in the laboratory to purify gases, and in the chemical industry for purification of gases or separation of gas mixtures (Table). Since the substance exchange in A. occurs via the contact surfaces of the two phases, apparatus is used to provide the largest possible surface area between the gas and liquid, such as columns packed with inert filler, spray towers, thin-layer absorbers, etc.

Industrial absorbtion processes

Gas to be removed	Absorption agent	Process
CO_2, COS and H_2S from natural, city and synthesis gas	Water	
	potassium carbonate solution	
	Methanol	Rectisol
	Sodium sarcosinate solution	Sulfosolvane
	Sulforlane/ diisopropanolamine	Sulfinol
	N-Methylcaprolactam	Gasolane
H_2O vapor	Glycols	
Ethylene	Acetone	
	Dimethylformamide	
	Methylpyrrolidone	
NH_3	Water	
SO_3	Conc. sulfuric acid	
CO	Cu salt/NH_3H_2O	Uhde

2) A. of radiation: Decrease in the intensity of electromagnetic (see Electromagnetic spectrum) or particulate radiation on passage through a solid, liquid or gas. A. involves transformation of some of the energy of the radiation into another form of energy, such as heat or energy of excitation. The ratio of absorbed (I_A) to incident (I_0) radiation is called the ***absorption***. The expression $I_A/I_0 \cdot 100$ is called the percent A.

If monochromatic radiation passes through a homogeneous substance in a parallel beam, then equal fractions of the radiation are absorbed by layers of equal thickness. For example, if visible radiation of a given wavelength is reduced in intensity by one half by passing through 1 cm of the substance, then of the remaining half, half will be absorbed by the next 1-cm layer, so that 1/4 of the original intensity remains. The absorption law $I_D = I_0 e^{-\alpha d}$ was first formulated by Lambert and Bouguer; here I_D is the intensity of the transmitted radiation, and I_0 is that of the incident radiation. Usually, the absorption law is expressed in the form $\ln(I_0/I_D) = \alpha d$, or, if base-10 logarithms are used, $\log(I_0/I_D) = k \cdot d$, where $k = 0.43422\ \alpha$. The absorption coefficient depends greatly on the frequency of the radiation and on the nature of the sample. A. is the basis of radiation chemistry and photochemistry. The A. in solutions is discussed in the entry on the Lambert-Beer law (see).

Absorption spectrum: see Spectrum.

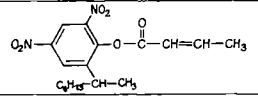
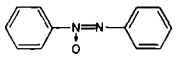
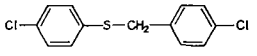
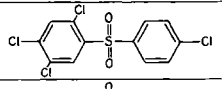
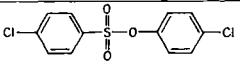
ABS plastics: see Polystyrenes.

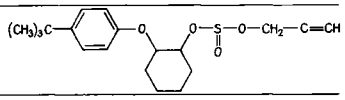
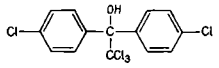
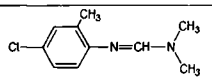
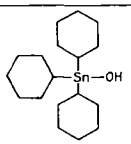
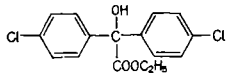
Ac: symbol for Actinium.

Acaricides: compounds used to combat plant-damaging mites, especially spider mites. The use of insecticides often destroys the natural enemies of mites, without eradicating the mites themselves. Since mites have very short generation times, and quickly develop resistance to chemicals, their control has become a problem. Preparations are needed which are specific for mites, and which have different mechanisms of action so that they can be used in rotation to prevent resistance from developing. A. are classified as ovicides, larvicides and adulticides.

The most important specific A. are dinitrophenol derivatives, azo compounds, sulfides, sulfones, sulfonate esters, sulfonite esters, diphenylcarbinols, carbamates, formamidines and organotin compounds (Table). Many Organophosphate insecticides (see) and Fungicides (see) effective against true mildew also have acaricidic effects.

Main types of acaricides

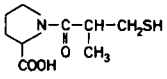
Name (Mechanism of action)	Formula
Dinocap (Contact acaricide, fungicide for true mildew)	
Fenazox (Fentoxan®) (Ovicide, larvicide, insecticide against white flies)	
Chlorbenzide (Ovicide, larvicide)	
Tetradifon (Ovicide, larvicide)	
Chlorfenson (Ovicide)	

Name (Mechanism of action)	Formula
Propargite (Ovicide, larvicide, adulticide)	
Dicofol (Contact acaricide, specific for soft-skinned mites)	
Chlorodimeform (Ovicide)	
Cyhexatin (Larvicide, adulticide)	
Chlorbenzilate (Acts against all stages of spider mites)	

Acceptor number, abb. ***AN***: a measure of the electrophilicity of a solvent. The A. is equal to the ^{31}P chemical shift δ_{corr} of a complex of the solvent with triethylphosphine oxide, relative to the ^{31}P chemical shift of a 1:1 adduct of triethylphosphine oxide:antimony(V) chloride (δ_{corr} = 100) in 1,2-dichloroethane. The A. is related to other parameters which characterize solvents (Z, E_T, Y values, free solvation enthalpies of anions, redox potential of hexacyanoferrate(III)/hexacyanoferrate(II) in the solvent). Together with the Donicity (see), the A. is a useful criterion for selection of a solvent for a chemical reaction.

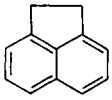
Acceptor substituent: atoms or groups of atoms which draw electron density to themselves from the molecule of which they are part. This can happen through an inductive effect (I-substituent) or a resonance effect (R-substituent).

ACE inhibitors: substances which reduce the activity of Angiotensin Converting Enzyme. This enzyme is present in blood plasma and converts the decapeptide angiotensin I into the octapeptide angiotensin II; the latter has a vasopressor effect. A. such as captopril and enalpril are used to reduce blood pressure.

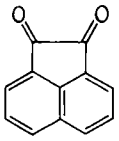


Captopril

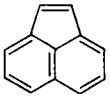
Acenaphthene, ***1,2-Dihydroacenaphthylene***: a *peri*-condensed aromatic hydrocarbon. A. crystallizes in colorless needles: m.p. 96.2 °C, b.p. 279 °C, n_D^{95} 1.6048. It is insoluble in water and soluble in organic solvents. A. is present in coal tar and can be isolated from it. It can be synthesized from naphthalene and ethene or from 1-ethylnaphthalene by heating to high temperatures. A. is oxidized on an industrial scale to the yellow acenaphthene quinone, which is used for a dye. It is also used in the manufacture of plastics, insecticides and fungicides. Under extreme conditions naphthalene-1,8-dioic acid can be obtained from A.



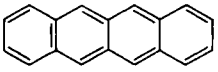
Acenaphthene quinone: a quinone derived from acenaphthene. A. forms yellow crystals, m.p. 261 °C. It is soluble in alcohol and benzene, and can be synthesized by oxidation of acenaphthene with hydrogen peroxide in glacial acetic acid. A. has insecticidal and fungicidal properties; it can be used as an intermediate in the synthesis of dyes.



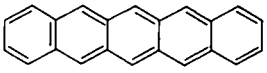
Acenaphthylene: a *peri*-condensed aromatic hydrocarbon. A. forms colorless crystals, m.p. 92 °C, b.p. 260 °C. A. is found in coal tar and can be isolated from it. Hydrogenation yields the industrially important acenaphthene.



Acenes: condensed aromatic hydrocarbons with linear arrangements of 2, 3, 4, 5 or 6 benzene rings. Naphthalene (see) and Anthracene (see) are followed by tetracene (naphthacene), a yellow-orange compound, pentacene (blue-violet) and hexacene (dark green). The aromatic character of the compounds decreases rapidly as the number of rings increases; they behave increasingly like conjugated polyenes instead. This results in the colors and sensitivity to oxygen and light.



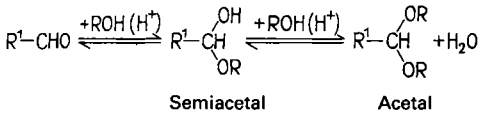
Tetracene



Pentacene

Acephate: see Organophosphate insecticides.

Acetal: an organic compound with the general formula $R^1R^2C(OR^3)_2$. Formally, A. can be seen as diethers of the normally unstable geminal diols (see Erlenmeyer rule). A. are obtained by reaction of aldehydes with alcohols in the presence of acid catalysts. The reaction goes primarily via the semiacetals, which in rare cases can be isolated:



A. are decomposed to the starting materials by aqueous acids. The A. of ketones generally cannot be obtained by direct addition of alcohols to ketones, because the addition equilibrium lies almost entirely on the side of the reactants. Ketone A. can be obtained by reaction of ketones with orthoformate esters:

$$R^1R^2C{=}O + HC(OR)_3 \xrightarrow{(H^+)} R^1R^2C(OR)_2 + HCOOR.$$

This method is also preferable to direct addition of the alcohol to α,β-unsaturated aldehydes.

Most A. are colorless, pleasant-smelling liquids. They are very stable to bases, and do not react with the common reagents for carbonyl detection under basic conditions. A. are thus a protected form of the aldehydes and ketones, and are often used instead of their parent compounds in organic reactions. In addition, they are used as solvents, softeners and perfumes.

Acetaldehyde, ***ethanal***: CH_3-CHO, a colorless, unstable liquid with a pungent smell. m.p. - 123.5 °C, b.p. 20.8 °C, n_D^{20} 1.3316. A. is infinitely soluble in water, alcohol and ether. It is easily ignited and burns with a pale flame. In higher concentrations, A. irritates the respiratory mucosae and has a narcotic effect on the central nervous system. In the presence of a small amount of conc. sulfuric acid it trimerizes spontaneously to Paraldehyde (see); at 0 °C the solid Metaldehyde (see) is formed.

Oxidizing agents convert A. to acetic acid; it can be reduced or hydrogenated to form ethanol. In the presence of dilute alkali or alkaline earth hydroxides, A. is converted by an Aldol reaction (see) to Acetaldol (see). In addition, it displays all the addition and condensation reactions typical for Aldehydes (see).

Occurrence. In nature, A. occurs mainly as an intermediate in the biological degradation of carbohydrates.

A. is obtained by oxidation or dehydrogenation of ethanol with oxygen or a silver contact, or with potassium dichromate and sulfuric acid. Industrially, the most common methods are water addition to acetylene in the presence of mercury salts, direct oxidation of ethene in air in the presence of palladium(II) and copper(II) chloride, and by hydrolysis of vinyl methyl ether, which is made industrially from acetylene and methanol.

Applications. A. is an important starting material for industrial production of an entire series of intermediates and end products, such as ethanol, acetic acid and its anhydride, acetaldol, crotonaldehyde, butadiene, acrolein, pentaerythritol, chloral hydrate and aldehyde resins.

Acetaldol, ***3-hydroxybutanal, 3-hydroxy-n-butaldehyde***, for short, ***aldol***: CH_3-CH(OH)-CH_2-CHO, a colorless, viscous liquid, b.p. 83 °C at $2.67 \cdot 10^3$ Pa, n_D^{20} 1.4238. A. is soluble in water and most organic solvents. Like all Aldehydes (see), A. is very reactive. In the presence of acids, it forms crotonaldehyde by splitting out water. A. is produced by aldol addition of acetaldehyde, usually under basic conditions. It is used as a hardener for gelatins and as an intermediate in the production of maleic acid and amino alcohols; it is also used in one method of butadiene synthesis. It is a sedative and narcotic.

Acetamide: CH_3-CO-NH_2 forms colorless and odorless deliquescent crystals, m.p. 82.3 °C, b.p. 221.2 °C. There is also a metastable form of A. which melts at 69 °C. A. is readily soluble in water and alcohol, and barely soluble in ether. It can react either as a weak base or as a very weak acid. It forms addition compounds with strong mineral acids, and ionic compounds of the general formula CH_3-CO-NHM^I with highly electropositive metals. Addition of water forms ammonium acetate, and elimination of water forms acetonitrile:

$$CH_3\text{–}CO\text{–}NH_2 + H_2O \longrightarrow CH_3\text{–}COONH_4$$

$$CH_3\text{–}CO\text{–}NH_2 \xrightarrow[-H_2O]{} CH_3\text{–}C{\equiv}N$$

A. is produced by heating of ammonium acetate, by reaction of ammonia with acetic anhydride, acetic acid or acetyl chloride, or by partial hydrolysis of acetonitrile. A. is used in the leather, textile and paper industries. In addition it is an intermediate for the preparation of pharmaceuticals and is used to accelerate vulcanization.

Acetanilide: $C_6H_5NHCOCH_3$, a derivative of aniline; colorless crystals, m.p. 114 °C. It is formed by acetylation of aniline. It was the first synthetic analgesic, introduced as "Antifebrin", but is no longer used in human medicine. It is used in the manufacture of other drugs and of dyes, as a stabilizer for H_2O_2 solutions and as an addition to cellulose ester varnishes.

Acetate fibers: synthetic fibers made by acetylation of cellulose with acetic acid/acetic anhydride and spinning of the acetone-soluble acetates (see Cellulose acetates, synthetic fibers, Table).

Acetates: salts and esters of acetic acid with the general formula CH_3-$COOM^I$ or CH_3-COOR. M^I symbolizes an ammonium residue or a monovalent metal, and R an aliphatic, aromatic or heterocyclic residue.

The salts are formed by reaction of ammonia, ammonium or metal hydroxides or carbonates with acetic acid; or by reaction of acetic acid with strongly electropositive metals, which evolves hydrogen. Basic and neutral A. can be formed with multivalent metals, e.g. CH_3-COO(OH)Mg and $(CH_3\text{-}COO)_2Mg$. Ammonium, sodium and aluminum acetates are important compounds used as preservatives, antiseptics, buffers, caustics, etc.

The esters of acetic acid can be produced by reaction of the corresponding alcohols with acetic acid, acetyl chloride or ketene. Some esters are synthesized by special methods. They are used mainly as solvents for fats, oils, laquers, resins, cellulose nitrate, chlorinated rubber, celluloid and colophony, and also as perfumes.

Acetazolamide: see Diuretic.

Acetic acid, ***ethanoic acid***: CH_3-COOH, the most important monocarboxylic acid, a colorless, combust-

ible, hygroscopic liquid with a pungent odor; m.p. 16.6 °C, b.p. 117.9 °C, n_D^{20} 1.3716. Anhydrous A. is also called ***glacial acetic acid***. It is readily soluble in water and most organic solvents. A.-air mixtures with 4 to 17 vol. % A. are explosive. Like many other Monocarboxylic acids (see), pure A. exists as hydrogen-bonded dimers in both the liquid and gas states. It is a weak acid; its salts and esters are called Acetates (see).

A. is rather stable to oxidation, and is often used as a solvent for oxidation reactions. It undergoes the reactions typical of aliphatic carboxylic acids, that is, it can be converted by suitable reagents into derivatives and substitution products. The reaction of perhydrol (30% aqueous solution of hydrogen peroxide) with A. forms ***peroxyacetic acid***, $CH_3CO\text{-}OOH$; this is used as a disinfectant. Pyrolysis of A. at 350 to 400 °C in the presence of alkaline catalysts generates ***acetone***, and Ketene (see) is formed on phosphorus-containing contacts at 700 °C: $CH_3\text{-}COOH \rightarrow CH_2{=}C{=}O + H_2O$. Addition of A. to acetylenes yields the Vinyl acetates (see). A. can be detected qualitatively by the *cacodyl reaction*, in which it forms cacodyl oxide with arsenic(III) oxide; cacodyl oxide has a strong, unpleasant odor.

A. is found in nature in both free and bound form. It is a component of many plant juices, essential oils and animal secretions. Its esters are found in some essential oils. A. is formed as the stable end product of fermentation and rotting of plant and animal material. It has an important role in metabolism in the form of acetyl-coenzyme A. A. can be obtained by ***vinegar fermentation*** from alcohol or by pyrolysis of wood. It is produced industrially by oxidation of acetaldehyde or butane in the presence of manganese or cobalt salts, or by carbonylation of methanol in the presence of cobalt(II) iodide at 150 °C and about 2 to 5 MPa, or in the presence of rhodium complex catalysts (see Catalysis): $CH_3\text{-}OH + CO \rightarrow CH_3\text{-}COOH$. More concentrated A. is produced by various dehydration methods, such as azeotrope distillation or liquid-liquid extraction; glacial acetic acid is obtained by the reaction of anhydrous sodium acetate with conc. sulfuric acid. A. is used as a solvent, to remove calcium from hides, as a reagent in dyeing and other textile treatments, and as a coagulant for latex. It is also an intermediate in the production of aromas, pharmaceuticals, dyes, acetates, acetic anhydride, acetyl chloride and table vinegar.

Acetic anhydride: $(CH_3\text{-}CO)_2O$, a colorless, lacrimatory liquid with a pungent odor; m.p. -73.1 °C, b.p. 139.55 °C, n_D^{20} 1.3906. A. is soluble in cold alcohol, ether and benzene. It is slowly solvolyzed in water or alcohol to acetic acid or acetate ester. A. is a suitable acetylation agent for alcohols, CH-acidic compounds, aromatic hydrocarbons and primary and secondary amines, e.g. $R\text{-}NH_2 + (CH_3\text{-}CO)_2O \rightarrow R\text{-}NH\text{-}CO\text{-}CH_3 + CH_3\text{-}COOH$. The methyl groups of A. are able to undergo condensation reactions due to the activating effects of the carbonyl groups. This reactivity is demonstrated, e.g. in the Perkin reaction (see) for preparation of cinnamic acid from benzaldehyde and A. A. is prepared industrially by two methods: in the *Wacher process* a ketene is prepared from acetic acid by intramolecular water elimination in the presence of phosphoric acid or phosphates at 700 to 750 °C; the ketene reacts with excess acetic acid to form A.: $CH_3\text{-}COOH \rightarrow CH_2{=}C{=}O + H_2O$; $CH_2{=}C{=}O + CH_3 \rightarrow (CH_3\text{-}CO)_2O$. In the second method, the *Knapsack process*, A. is made by oxidation of acetaldehyde in the presence of metal salts at 40 to 60 °C. In this synthesis the first product is peracetic acid, which reacts further with excess acetaldehyde to the end product: $CH_3\text{-}CHO + O_2 \rightarrow CH_3\text{-}CO\text{-}OOH$; $CH_3\text{-}CO\text{-}OOH + CH_3\text{-}CHO \rightarrow (CH_3\text{-}CO)_2O + H_2O$. In the laboratory, A. can be synthesized in high yields by reaction of sodium acetate with inorganic acid chlorides, e.g. thionyl chloride or phosphorus oxide chloride. These reactions form first acetyl chloride, which reacts with unreacted sodium acetate to form A. A. is used mainly as an acetylation reagent, e.g. in the production of cellulose acetate, drugs, dyes, flavorings and perfumes. In addition, A. is used as a solvent and condensing agent.

Acetoacetate ester syntheses: see acetoacetate esters.

Acetoacetic acid, ***3-oxobutanoic acid, β-ketobutyric acid***: $CH_3\text{-}CO\text{-}CH_2\text{-}COOH$, an aliphatic β-ketocarboxylic acid. A. is a colorless, syrupy liquid which gives a strongly acidic reaction; it can be crystallized only with difficulty. m.p. 36 to 37 °C. On heating, A. decomposes around 100 °C to form acetone and carbon dioxide: $CH_3\text{-}CO\text{-}CH_2\text{-}COOH \rightarrow CH_3\text{-}CO\text{-}CH_3 + CO_2$. A. is soluble in water, alcohol and ether. It is formed in the liver, starting from acetyl-coenzyme A, via acetoacetyl-coenzyme A, and in diabetics it is secreted into blood and urine as one of the ketone bodies (acetone is another). A. can be synthesized by hydrolysis of acetoacetate esters or by oxidation of butyric acid. Because of its low stability, it is used in organic syntheses only in special cases.

Acetoacetic acid ethyl ester: see Ethyl acetoacetate.

Acetoin, ***3-hydroxybutan-2-one***: $CH_3\text{-}CH(OH)\text{-}CO\text{-}CH_3$, one of the acyloins. A. is a colorless liquid; m.p. - 72 °C, b.p. 143 °C, n_D^{20} 1.4171. A. is soluble in water and acetone, insoluble in ether. It reduces Fehling's solution and dimerizes easily. Catalytic dehydration yields Methyl vinyl ketone (see). A. is made enzymatically from acetaldehyde or chemically by reduction of diacetyl.

Acetone, ***propanone, dimethyl ketone***: $CH_3\text{-}CO\text{-}CH_3$, a colorless, non-viscous, pleasant smelling, inflammable liquid. m.p. - 95.34 °C, b.p. 56.2 °C, n_D^{20} 1.3588. A. is miscible with water in all proportions, and miscible with most organic solvents. It is very stable to light and air. A. is found in volatile oils and in the urine of diabetics, where it can be detected with the Lieben iodoform test (see) or the Legal acetone test (see). The pathological accumulation of A. in urine is called *acetonuria*. A. is formed in the body via the ketone bodies. Like all Ketones (see), A. reacts with nucleophilic reagents, forming typical addition and condensation products. A. can be converted to isopropanol by reduction; and to bromoacetone by reaction with bromine.

Production. A. is formed in considerable amounts by dry distillation of wood, but its separation from other products, e.g. methanol, and purification is very tedious. A. can also be produced by pyrolysis of acetic acid on a manganese(II) oxide contact, or from

acetylene and water vapor in the presence of zinc oxide. The more modern methods of producing A. include dehydrogenation of isopropanol, the Hock process (see), in which A. is obtained as a byproduct from cumene, and the direct oxidation of propene in the presence of copper(II) chloride and palladium(II) chloride.

Applications. A considerable fraction of the A. produced is used as a solvent and extraction agent for resins, fats, oils, colophony, cellulose acetate, acetylene and the like. It is also becoming steadily more important in the production of derivatives like diacetone alcohol, mesityloxide, chloroform, etc.

Acetone cyanohydrin, ***α-hydroxyisobutyronitrile***: $(CH_3)_2C(OH)CN$, a colorless, inflammable liquid which smells like hydrogen cyanide. m.p. - 19 °C, b.p. 82 °C at $3.07 \cdot 10^3$ Pa; n_D^{20} 1.3996. A. is readily soluble in water, alcohol, chloroform and ether. It is obtained by addition of hydrogen cyanide to acetone in the presence of basic catalysts. Traces of alkali hydroxides cause it to split into the starting materials. This back reaction, which releases hydrogen cyanide, is responsible for the toxicity of A. A. is the starting material for methacrylate esters; it is also used as an insecticide.

α,α-Acetonedicarboxylic acid, ***3-oxopentanedioic acid***, ***β-ketoglutaric acid***: $HOOC\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}COOH$, a colorless, crystalline compound; m.p. 135 °C (dec.), which decomposes on distillation. It is readily soluble in water and alcohol, and slightly soluble in ether or chloroform. When stored, it slowly decomposes to acetone and carbon dioxide. When heated, or in the presence of mineral acids, metal salts or hydroxides, the cleavage occurs much faster. In every case, the unstable acetoacetic acid is formed as an intermediate:

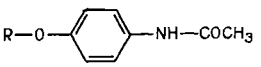
$$HOOC\text{–}CH_2\text{–}CO\text{–}CH_2\text{–}COOH \xrightarrow{-CO_2} CH_3\text{–}CO\text{–}CH_2\text{–}COOH \xrightarrow{-CO_2} CH_3\text{–}CO\text{–}CH_3$$

α,α-A. is formed by the action of fuming sulfuric acid on citric acid, by hydrolysis of 1,3-dicyanoacetone (obtained from 1,3-dichloroacetone and alkali cyanides), or from acetone and carbon dioxide. α,α-A. and its esters have several functional groups; the carboxyl or ester group, the keto group and the active methylene group can all undergo the reactions typical of these classes. α,α-A. is therefore useful for the syntheses of various heterocycles, e.g. some alkaloids. It is also used in the syntheses of amino acids, pharmaceuticals, insecticides, fungicides and disinfectants. Like all β-dicarbonyl compounds, α,α-A. forms chelate complexes with many metal ions, such as copper or iron, making it useful for the removal of traces of heavy metals from fats, oils and petroleum products.

Acetonitrile, ***methyl cyanide***: $CH_3\text{-}C{\equiv}N$, the simplest aliphatic nitrile. A. is a colorless, poisonous liquid with a pleasant odor; m.p. - 45.7 °C, b.p. 81.6 °C, n_D^{20} 1.3442. A. is infinitely soluble in water and most organic solvents. It burns with a bright pink flame. A. shows the reactions typical of aliphatic Nitriles (see). Because the nitrile group has an activating effect, the H-atoms of the methyl group undergo electrophilic substitution relatively easily. A. is contained in the crude benzene fraction of anthracite coal tar and in the liquid from low-temperature distillation of lignite coal. It can be synthesized according to Kolbe from methyl iodide and alkali-metal cyanides, by dehydration of acetamide or acetaldehyde oxime, and from acetylene and ammonia. Industrially, A. is obtained as a byproduct of acrylonitrile production through ammonoxidation of propylene. A. is used mainly as a solvent, but also as an intermediate in organic syntheses.

Acetonylacetone, ***hexane-2,5-dione***: $CH_3\text{-}CO\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_3$, the simplest 1,4-diketone. A. is a colorless liquid with an aromatic odor; m.p. - 5.5 °C, b.p. 194 °C, n_D^{20} 1.4421. It is soluble in water, alcohol, ether and acetone. It is produced by decarboxylation of diacetylsuccinic acid or by hydrolytic ring cleavage of 2,5-dimethylfuran. A. is used as a solvent for paints, laquers and cellulose acetate, and as a component in the synthesis of heterocyclic compounds.

Acetophenetidin, ***phenacetin***: 4-ethoxyacetacetanilide, a white, crystalline substance, m.p. 135 °C. A. can be made by the following steps: 1) nitration of chlorobenzene to 4-nitrochlorobenzene (and other products), 2) substitution of an ethoxy group for the activated Cl atom, forming 4-nitroethyoxybenzene, 3) reduction of the nitro group and 4) acetylation of the resulting amino group. It was introduced in 1887 as an analgesic. Kidney damage can result from long-term consumption of high doses. 4-Hydroxyacetanilide (white crystals, m.p. 168 °C) was introduced into pharmacy as *paracetamol* after it was found to be one of the biotransformation products of A., and the pain-killing effects were ascribed to it.

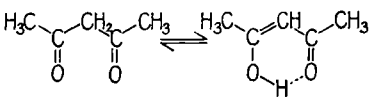


R = C_2H_5: Acetophenetidin
R = H: Paracetamol

Acetophenone, ***methyl phenyl ketone, acetylbenzene***: $C_6H_5\text{-}CO\text{-}CH_3$, a colorless compound with an aromatic odor. m.p. 20.5 °C, b.p. 202.6 °C, n_D^{20} 1.5372. A. is insoluble in water, but dissolves readily in most organic solvents. It is synthesized mainly through the Friedel Crafts reaction (see) or by catalytic oxidation of ethyl benzene. A. is used as a solvent, as a starting material for production of formaldehyde resins, pharmaceuticals, dyes and perfumes. It was formerly used as a hypnotic.

Acetyl-: term for the $CH_3\text{-}CO\text{-}$ group in a molecule, for the unstable radical $CH_3\text{-}CO\cdot$ and for the cation $CH_3\text{-}CO^+$.

Acetylacetone, ***pentane-2,4-dione***: $CH_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3$, the simplest aliphatic 1,3- or β-diketone. A. is a colorless, non-viscous liquid with a pleasant odor; m.p. - 23 °C, b.p. 140 °C, n_D^{20} 1.4494. A. is very soluble in water and most organic solvents. Like all 1,3-dicarbonyl compounds, it undergoes Keto-enol tautomerism (see).



Keto form Enol form

In the liquid state at 20 °C, 18% is in the keto form, and 82% in the enol form. In the vapor phase, it is nearly 100% in the enol form. Chelate acetylacetonates derived from the enol form are formed with metal salts. A. can be produced by acetylation of acetoacetate or acetone with acetic anhydride and boron trifluoride; or by pyrolysis of isopropylacetate. A. is used as a solvent, in the production of nitrogen-containing heterocycles in the pharmaceutical industry, and for the production of dyes and pesticides. It is also used in the plastics industry as a stabilizer, initiator of polymerization and hardener.

Acetyl acetic acid: same as Acetoacetic acid.

Acetylation: a preparative method for introduction of an acetyl group, CH_3-CO-, into an organic compound. A. is one of the most commonly used reactions for Acylation (see). Compounds with acidic H-atoms, such as alcohols, phenols, thiols, primary and secondary amines, are often acetylated to protect them from undesired side reactions. A. is used to determine the number of hydroxy, sulfhydryl or amino groups in organic compounds, the Acyl number (see). The A. of arenes in the Friedel-Crafts reaction (see) produces acetyl-substituted aromatics.

Acetylbenzene: see Acetophenone.

Acetylbromide: CH_3-CO-Br, a colorless liquid which fumes strongly in air; m.p. - 98 °C, b.p. 76 °C, n_D^{20} 1.4537. A. slowly turns yellow under long storage. It is readily soluble in ether, acetone, benzene and chloroform, but is solvolyzed by water or alcohol to form acetic acid or acetate esters. It is synthesized by reaction of phosphorus pentabromide with acetic acid. A. is used mainly as an acetylation agent in organic syntheses.

Acetylcellulose: see Cellulose acetate.

Acetylchloride, ***ethanoyl chloride***: CH_3-CO-Cl, a colorless liquid with a suffocating smell which is very irritating to the eyes and respiratory passages; m.p. - 112 °C, b.p. 50.9 °C, n_D^{20} 1.3897. On exposure to moist air, A. is hydrolysed with fuming, forming acetic acid and hydrogen chloride. It is soluble in most organic solvents. A. is a very reactive compound which forms acetamide with ammonia, acetate esters with alcohols, and *N*-substituted acetamides with primary and secondary amines. It is produced by reaction of acetic acid or its alkali salts with inorganic acid chlorides, e.g. sulfuryl chloride, thionyl chloride, phosphoryl chloride, phosphoryl oxochloride, etc. A. is produced industrially by reaction of hydrogen chloride with acetic anhydride; it is used mainly as an acetylation agent in organic synthesis. It is also used as a reagent in analytical organic chemistry for quantitative determination of hydroxy groups and to distinguish tertiary amines from primary and secondary amines.

Acetylcholine: 2-acetoxyethyl trimethylammonium hydroxide, the ester of choline with acetic acid. The neutral chloride, $[(CH_3)_3N^+$-CH_2-CH_2-O-CO-$CH_3]Cl^-$, is stable. A. is a neurotransmitter. It is administered parenterally in treatment of arterial blockage.

Acetylcholinesterase: an enzyme (see Esterases) which catalyses the cleavage of acetylcholine into choline and acetate ion. It is found in nervous tissue and is responsible for removal of acetylcholine released into the synapses during propagation of nervous impulses from one nerve cell to another.

A serine and a histidine residue are required for activity of A. The catalytically active serine hydroxyl is blocked by organophosphates, which inhibit the esterase activity. The enzyme can be reactivated by pralidoxime chloride (2-[(hydroxyimino)methyl]-1-methylpyridinium chloride), which is therefore used as an antidote to organophosphate poisoning.

Acetylcholinesterase inhibiters: see Parasympatheticomimetica.

Acetyl-coenzyme A: see Coenzyme A.

Acetylene: see Ethyne.

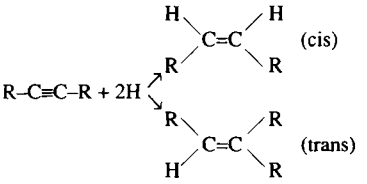
Acetylenecarboxylic acid: same as Propiolic acid.

Acetylene chemistry: a collective term for all chemical reactions starting from ethyne (acetylene). Ethyne is the parent compound of a very large number of organic compounds, so that it, together with petroleum and coal, is a basis for modern industrial organic chemistry. The development of A. occurred in two stages; the first was the work of Berthelot, Dupont, Nieuwland, Carothers, Hilebrone and Kutscherov, who discovered how to make acetaldehyde and its derivatives (acetic acid, ethyl acetate, acetic anhydride, acetone, ethanol, crotonaldehyde and butanol) from ethyne.

The second stage, which is extremely important to industry, is called ***Reppe chemistry*** after its founder, W. Reppe. Reppe opened a new field of A. by introducing pressure synthesis. He avoided the danger of explosion of the compressed ethyne by careful engineering. In addition to the high pressures, catalysts such as heavy metal acetylides, metal carbonyls and hydrogen metal carbonyls, are very important. The following reactions are especially significant:

1) *Hydration* of ethyne in the presence of 15% sulfuric acid with mercury(II) sulfate as catalyst leads via the unstable vinyl alcohol to acetaldehyde, the most important intermediate in A.: $HC{\equiv}CH + H_2O \rightarrow [H_2C{=}CHOH] \rightarrow CH_3$-CHO. When homologs of ethyne are used, ketones are formed; this hydration is a special case of vinylation.

2) *Catalytic hydrogenation* of ethyne and its homologs leads either to the corresponding alkane, or the C≡C triple bonds can be selectively converted to C=C double bonds with deactivated catalysts. The Lindlar catalyst, a palladium-calcium carbonate poisoned with lead, is used for this. The hydrogen transfer occurs by *cis*-addition; double bonds are not attacked by this method: R-C≡C-CH=CH-R + 2 H → R-CH=CH-CH=CH-R. Selective hydrogenation to the alkene is also possible with sodium in liquid ammonia, in which case *trans*-addition occurs:



3) *Addition of halogens*, e.g. chlorine or bromine, can be accelerated by Lewis acids or initiated by light. The reaction is a stereoselective *trans*-addition to 1,2-disubstituted ethenes, and further reaction produces

1,1,2,2-tetrahaloethane. This is converted to trihalooethene by elimination of hydrogen halide:

$$HC{\equiv}CH \xrightarrow{Cl_2} H(Cl)R{=}R(Cl)N \xrightarrow{Cl_2} HC(Cl)_2{-}C(Cl)_2H \xrightarrow{-HCl} HC(Cl){=}CCl_2$$

Trichloroethene is an important solvent.

4) *Dimerization* of ethyne with ammonium and copper(I) chlorides as catalysts produces vinylethyne, the starting material for chloroprene: $CH_2{=}CCl{-}CH{=}CH_2$.

Reppe syntheses include:

5) *Vinylation*. In addition to hydrogen halides and water, alcohols, phenols, thiols, amines, carboxylic acids and hydrogen cyanide add to ethyne to produce various types of vinyl compound. a) The addition of hydrogen chloride to ethyne at 140 to 200 °C in the presence of a mercury(II) chloride/activated charcoal catalyst produces vinyl chloride by the reaction: $HC{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$; the product is used to make PVC. b) Addition of acetic acid to ethyne at 170 to 200 °C in the presence of a zinc acetate/activated charcoal or mercury(II) chloride catalyst produces vinyl acetate, which can be saponified to vinyl alcohol: $HC{\equiv}CH + CH_3COOH \rightarrow CH_2{=}CH{-}OOCCH_3$. c) Addition of hydrogen cyanide to A. yields the starting material for polyacrylonitrile fibers, acyl nitrile: $CH{\equiv}CH + HCN \rightarrow H_2C{=}CH{-}CN$. d) Vinyl ethers are formed by addition of alcohols to ethyne using alkaline catalysts: $HC{\equiv}CH + ROH \rightarrow H_2C{=}C{-}OR$.

Ethynylations are reactions of ethyne with aldehydes or ketones which maintain the triple bond. Copper(I) salts, including copper acetylide, are used as catalysts. Ethyne reacts with formaldehyde to form propargyl alcohol and but-2-yne-1,4-diol, which can be made into butadiene after hydrogenation to butane-1,4-diol, and with acetone to form 3-methylbut-1-yn-3-ol, from which isoprene can be made:

$$HC{\equiv}CH + HCHO \longrightarrow HC{\equiv}C{-}CH_2{-}OH + HCHO \longrightarrow HO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OH;$$
$$HC{\equiv}CH + CH_3{-}CO{-}CH_3 \longrightarrow HC{\equiv}C{-}C(OH)(CH_3)_2.$$

The aminomethylation and the dimerization of ethyne to vinyl acetylene are also ethynylation reactions and are industrially significant.

7) In *carbonylations*, ethyne and carbon monoxide react in the presence of compounds with reactive hydrogen, e.g. water, alcohol or secondary amines, to acrylic acid or its derivatives: $HC{\equiv}CH + CO + H_2O \rightarrow CH_2{=}CH{-}COOH$ (acrylic acid), $HC{\equiv}CH + CO + ROH \rightarrow CH_2{=}CH{-}COOR$ (acrylic esters), $HC{\equiv}CH + CO + R_2NH \rightarrow CH_2{=}CH{-}CONR_2$ (acrylamide). Carbonylation occurs under pressure with carbonyl-forming metals, e.g. cobalt, nickel or iron, as catalysts.

8) *Cyclization* of ethyne in the presence of tricarbonyl(triphenylphosphine)nickel at 60 to 70 °C gives a mixture of benzene (88%) and styrene (12%). In the presence of nickel(II) cyanide and tetrahydrofuran, cyclooctatetraene is formed in 70% yield, along with other products.

Reactions 1 to 3 and 5c are uneconomical, and the corresponding products can be produced more cheaply from ethene, or in the case of acrylonitrile, through ammonoxidation of propene. A. has been partially displaced by ethylene chemistry. However, there has been a renaissance of carbochemistry, and ethyne and products of Reppe syntheses have again achieved great industrial importance. Vinyl ether is now produced exclusively from ethyne, and there is no competition for the synthesis of butyne-1,4-diol or butane-1,4-diol from ethyne.

Acetylene dicarboxylic acid, ***butynedioic acid***: $HOOC{-}C{\equiv}C{-}COOH$, the simplest dicarboxylic acid with a $C{\equiv}C$ triple bond. The crystals are colorless platelets, m.p. 179 °C. A. is very slightly soluble in water, alcohol and ether. It can be synthesized by dehydrobromination of dibromosuccinic acid. The diesters of A. are important as intermediates in the production of heterocycles and as dienophiles in Diels-Alder reactions.

Acetylene soot: soot produced by incomplete combustion of acetylene.

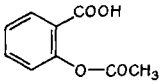
Acetylene tetrachloride: same as 1,1,2,2-Tetrachloroethane.

Acetylides: see Ethyne.

3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione: same as Dehydroacetic acid.

O-Acetylphenol: same as Phenyl acetate.

Acetyl salicylic acid, ***aspirin***: the crystals are colorless needles with a sour taste; m.p. 137 °C. A. is made by acetylation of salicylic acid. As a phenol ester, it is very sensitive to hydrolysis. It is very widely used as an analgesic and antipyretic. A. is less damaging to the gastric mucosa than salicylic acid. A. inhibits thrombocyte aggregation, by inhibiting the enzymes of prostaglandin synthesis. Since thrombocytes initiate blood coagulation, A. also inhibits clot formation, and this property has been utilized therapeutically in recent years. To prevent embolisms, A. is administered as tablets from which it is continuously released during passage through the intestinal tract (Micristin®, Colfarit®).



N'-Acetylsulfanilamide: see Sulfonamide.

Acheson process: see Graphite.

Achiral: see Stereoisomerism, 2.

Acid: see Acid-base concepts; Nomenclature, sect. II E.

Acid anhydride: see Carboxylic acid anhydride.

Acid-base concepts: systems based on definitions of acids and bases which permit classification of many compounds and interpretation of their reactions within a unified conceptual framework. The concept of acids and bases has undergone many changes in the course of its development. The definitions were generalized in several stages to include a broader range of compounds, and in addition, different definitions evolved from the application of the concept to different areas.

Arrhenius acids and bases: In 1887 Arrhenius defined acids as substances which dissociate to form H^+ ions in aqueous solutions, and bases as substances which dissociate to form OH^- ions in aqueous solutions. The reaction of an acid with a base is called

Important conjugate acid-base pairs with their pK_a and pK_b values

Acid strength	pK_a	Acid	+ H_2O ⇌ H_3O^+ + Base	pK_b	Base strength
Very strong	− 10	$HClO_4$	+ H_2O ⇌ H_3O^+ + ClO_4^-	24	Very weak
	− 10	HI	+ H_2O ⇌ H_3O^+ + I^-	24	
	− 9	HBr	+ H_2O ⇌ H_3O^+ + Br^-	23	
	− 6	HCl	+ H_2O ⇌ H_3O^+ + Cl^-	20	
	− 3	H_2SO_4	+ H_2O ⇌ H_3O^+ + HSO_4^-	17	
	− 1.74	H_3O^+	+ H_2O ⇌ H_3O^+ + H_2O	15.74	
Strong	− 1.32	HNO_3	+ H_2O ⇌ H_3O^+ + NO_3^-	15.32	Weak
	1.92	HSO_4^-	+ H_2O ⇌ H_3O^+ + SO_4^{2-}	12.08	
	1.96	H_3PO_4	+ H_2O ⇌ H_3O^+ + $H_2PO_4^-$	12.04	
	3.14	HF	+ H_2O ⇌ H_3O^+ + F^-	10.86	
Medium	4.76	CH_3COOH	+ H_2O ⇌ H_3O^+ + CH_3COO^-	9.24	Medium
	5.52	H_2CO_3	+ H_2O ⇌ H_3O^+ + HCO_3^-	7.48	
	6.92	H_2S	+ H_2O ⇌ H_3O^+ + HS^-	7.08	
Weak	9.21	NH_4^+	+ H_2O ⇌ H_3O^+ + NH_3	4.79	Strong
	9.40	HCN	+ H_2O ⇌ H_3O^+ + CN^-	4.60	
	12.90	HS^-	+ H_2O ⇌ H_3O^+ + S_2^{2-}	1.10	
Very weak	15.74	H_2O	+ H_2O ⇌ H_3O^+ + OH^-	− 1.74	
	23	NH_3	+ H_2O ⇌ H_3O^+ + NH_2^-	− 9	
	34	CH_4	+ H_2O ⇌ H_3O^+ + CH_3^-	− 20	

Neutralization (see); the essential process is the combination of H^+ and OH^- ions to form water molecules. The neutral point (see Ion product) is a state in which the H^+ and OH^- concentrations are equal. The strength of an acid or base corresponds to the dissociation constant of the compound in water. The disadvantages of this definition are that it is limited to aqueous systems, and that there are compounds which do not contain OH^- groups, but have the ability to neutralize acids, e.g. ammonia, organoelement compounds, etc., which are not included in the definition of bases. The Arrhenius concept has now been replaced by the Brönsted system.

Brønsted acids and bases: Brønsted and Lowry independently and simultaneously (1923) defined acids as systems which can donate protons, and bases as systems which can accept protons. This essentially functional definition includes charged particles, and a distinction is therefore made between *neutral* acids (e.g. H_2SO_4, HNO_3) and bases (e.g. NH_3, H_2O), *anionic* acids (e.g. HCO_3^-, $H_2PO_4^-$) and bases (e.g. HCO_3^-, OH^-), and *cationic* acids (e.g. NH_4^+, OH_3^+) and bases (e.g. $[Al(OH)(H_2O)_5]^{2+}$). Acids which can donate one proton are called *monoprotic* (e.g. HNO_3, HCl, $HClO_4$); those which can donate two protons are *diprotic* (e.g. H_2SO_4, H_2CO_3), and those which can donate three, *triprotic* (e.g. H_3PO_4, H_3AsO_4). Di- and triprotic acids can form acidic salts after partial dissociation. Similarly, *monoacidic bases* (e.g. OH^-) can accept one proton, and *diacidic bases*, two (e.g. O^{2-}, SO_4^{2-}, HPO_4^{2-}).

The Brønsted concept is not limited to aqueous systems, but can be applied to reactions in non-aqueous solvents and the gas phase.

Since protons never exist in the free state, the dissociation of an acid (*proton donor*) must always occur in the presence of a base (*proton acceptor*). The proton transfer process is called *protolysis*. When an acid donates a proton, the remaining part of the compound is naturally able to accept a proton, and is thus a base; the original base, having accepted a proton, has been transformed into an acid: acid HA + base B ⇌ Base A^- + acid HB^+. If the only difference between the acid and base is the presence of the proton on the acid, they constitute a *conjugate acid-base pair*. For example, the chloride ion is the base corresponding to the acid HCl, and the ammonium ion is the acid corresponding to the base NH_3 (Table).

Compounds which can act either as acids or as bases are called *Ampholytes* (see) (e.g. HCO_3^-, HPO_4^{2-}, H_2O, NH_3). Amphoteric behavior is a necessity for *autoprotolysis (acid-base disproportionation)*, i.e. the ability of a system to protonate itself, e.g. $HPO_4^{2-} + HPO_4^{2-} \rightleftharpoons H_2PO_4 + PO_4^{3-}$. The autoprotolysis equilibrium for water according to the equation $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ is of fundamental importance for an understanding of many processes which occur in water (see pH, Ion product).

If the strength of an acid or base is to be described in terms of the extent of its dissociation, this dissociation must be related to an interaction with a standard base or acid. Water, which is amphoteric, is suitable in most cases, and the *acid strength (acidity)* is described by the equilibrium constant for the reaction of the acid (HA) with water. This equilibrium constant is called the *acid constant* K_a, and its negative logarithm to the base ten is called its pK_a:

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$\frac{a_A \cdot a_{H_3O}}{a_{HA}} = K_a$$

$$pK_a = -\lg K_a;$$

Similarly, the measure of *base strength (basicity)* is the equilibrium constant of the reaction of the base (B) with water, the *base constant* K_b; the pK_b is the negative logarithm of K_b:

$$B + H \rightleftharpoons A + HO,$$

$$\frac{a_{BH^+} \cdot a_{OH^-}}{a_B} = K_B$$

$$pK_B = -\lg K_B.$$

Strong acids have large acid constants and small pK_a values, while weak acids have small acid constants and large pK_as; the relation between base constants and basicity is similar. The acid and base constants of a conjugate acid-base pair are inversely related to each other. Their product is equal to the ion product of water: $K_a \cdot K_b = K_w = 10^{-14}$; $pK_a = pK_b = pK_w = 14$ (see Ion product). In other words, a strong acid always has a weak conjugate base, while a weak acid always has a strong conjugate base. The pK values for some important conjugate acid-base pairs are listed in the table. This relationship makes it clear why, for example, strong acids are able to release weak acids from their salts, and why there is a considerable change in the pH when some salts are dissolved in water. For example, in the reaction of hydrochloric acid with sodium acetate, acetic acid is formed, because the acetate ion, as the strong conjugate base of weak acetic acid, binds the proton which the strong HCl is ready to donate. In other words, in the competition for protons, the CH_3COO^- is more successful than the Cl^- ion.

Similarly, with very strong acids the basicity of water is fully expressed, i.e. very strong acids completely transfer their protons to the water, and in so doing dissociate completely. This means that very strong acids cannot exist in water; they are always present in the form of H_3O^+ ions and their conjugate bases. Thus aqueous solutions of all very strong acids have the same acidity, due to the H_3O^+ ion, which is the strongest acid which can exist in water. This phenomenon is called the *leveling effect of water*. Likewise, stronger bases than the hydroxyl ion OH^- do not exist in water, but react immediately to form the conjugate acids and the OH^- ion. The protonation activity of extremely strong acids with respect to very weak bases can therefore be observed only in nonaqueous solutions (see Superacids).

If a salt is dissolved in water, its components, which always have acid-base properties, will always interact with the amphoteric water. For example, in aqueous sodium carbonate solutions, the strongly basic CO_3^{2-} ion binds protons from the water. Due to the constancy of the ion product of water, this causes a shift in pH toward the basic range. Similarly, ammonium salts, for example, give an acid reaction: the NH_3^+ ions, as the conjugate acid of the weak base ammonia, transfer some of their protons to the water.

Protolysis reactions of acids and bases with water determine the pH values of aqueous solutions. On the other hand, the protolysis equilibrium of the conjugate acid-base pair is determined by the pH of the solution (see Buffer solutions).

The Brønsted acid-base definition is extremely useful in treatment of proton-transfer reactions in water and nonaqueous solutions, especially in analytical chemistry, and is universally accepted. This is due in large part to the ease with which protolysis equilibria can be described in terms of this definition.

Lewis acids and bases: According to Lewis (1923), bases are molecules or ions which are able to donate an electron pair to a reaction partner to form a covalent bond, that is, they are *electron donors* and, depending on reaction kinetics, potential *nucleophiles*. Acids are molecules or ions which lack an electron pair and serve as *electron pair acceptors* and, seen kinetically, as *electrophiles*, which can form a covalent bond with a Lewis base. Thus any particle which has an unoccupied low-energy atomic or molecular orbital is a Lewis acid. The group includes cations in general (e.g. Ag^+, Cu^{2+}, Br^+, R_3C^+), molecules with incomplete electron octets (e.g. BF_3, $AlCl_3$, SO_3, $BeCl_2$), unsaturated coordinate compounds in which the central atom can undergo octet expansion (e.g. SiF_4, $SnCl_4$, PCl_3, SbF_5) and molecules with polar multiple bonds, in which the more positive atom carries the acidity (e.g. CO_2, carbonyl compounds). Correspondingly, *Lewis bases* are those particles which have occupied, relatively high-energy atomic or molecular orbitals. These include molecules with free electron pairs not used in bonding, anions (which act as bases with respect to metal cations or in complex formation) and molecules with polar multiple bonds in which the more negative atom acts as the center of basicity. Reactions between Lewis acids and bases yield neutralization products in which the components are joined by covalent bonds:

Acid	+ Base	⇌ Product
BF_3	+ NH_3	⇌ $F_3B{-}\overset{-}{N}H_3$
$AlCl_3$	+ Cl^-	⇌ $[AlCl_4]^-$
Ag^+	+ 2 NH_3	⇌ $[Ag(NH_3)_2]^+$
CO_2	+ OH^-	⇌ HCO_3^-
H^+	+ OH^-	⇌ H_2O

The Lewis definition of acids and bases has very wide applications, especially in discussions of reaction mechanisms in organic and coordination chemistry (HSAB concept, see below).

Although the Lewis and Brønsted base definitions include the same compounds, the definitions of acids are fundamentally different, and it is problematical that compounds which are usually classified as acids, e.g. HCl, H_2SO_4, H_3PO_4, etc., are not Lewis acids. To deal with this problem, Bjerrum proposed the following definition in 1951.

In the ***Bjerrum base-antibase system***, the term "acid" is reserved for proton donors, while Lewis acids are called *antibases*:

Base	+ Antibase	⇌ Product
NH_3	+ H^+	⇌ NH_4^+
Cl^-	+ $AlCl_3$	⇌ $[AlCl_4]^-$
S^2	+ SnS_2	⇌ SnS_3^{2-}

This definition can be extended to include a suggestion made by Lux (1939) and Flood (1947), that the proton transfer which is the basis of the Brønsted definition is only a special case of ion transfer reactions. Many reactions which occur in molten salts can be formulated as oxide ion transfers (*oxidotropism*). *Oxide ion donors* are defined as bases, and *oxide ion acceptors* as acids, and on this basis, corresponding base-antibase systems can be formulated, e.g.:

Base	⇌ Antibase	+ O^{2-}
CO_3^{2-}	⇌ CO_2	+ O^{2-}
2 SO_4^{2-}	⇌ $S_2O_7^{2-}$	+ O^{2-}

For example, the conversion of SiO_2 into nonrefractory form by fusion with a sodium-potassium carbonate mixture can thus be understood as a base-antibase reaction in which, as a result of an oxide ion transfer, the starting products are converted to the corresponding antagonists:

$$\underset{\text{Base + Antibase}}{CO_3^{2-} + SiO_2} \rightleftharpoons \underset{\text{Base + Antibase}}{SiO_3^{2-} + CO_2}$$

Ion-transfer reactions are also the basis of the ***solvent concept***, which was proposed by Gutmann and Lindquist (1939) and by Ebert and Konopik (1949), especially for reactions in aprotic solvents. According to this concept, acids are substances which increase the concentration of the cations typical of the solvent, while bases increase the concentration of solvent-typical anions. For example, in the phosphorus oxychloride system, which has the following dissociation reaction: $2\ POCl_3 \rightleftharpoons POCl_2^+ + POCl_4^-$, chloride ion donors would be bases, and chloride ion acceptors would be acids.

An even more inclusive generalization is the ***Ussanovitsch definition*** (1939), according to which acids are substances which react with bases, which cleave off protons or other cations (*cation donors*), or which can accept anions or electrons (*anion acceptors, electron acceptors, oxidation agents*). Bases are substances which react with acids, cleave off anions or electrons (*anion donors, electron donors, reduction agents*) or which can accept protons or other cations (*cation acceptors*). Thus this definition includes redox reactions as well as acid-base reactions, and in fact sees all chemical reactions, except for combination of radicals to form covalent compounds, as acid-base reactions.

In the ***HSAB concept*** (hard and soft acids and bases), which was published in 1963 by Pearson, an attempt is made to find criteria for the stability of the products of reactions of Lewis acids and basis. It turns out that the equilibrium position of the reaction

Lewis acid + Lewis base $\rightleftharpoons$ acid-base complex

depends primarily on the electronegativity and polarizability, i.e. on the deformability of the electron shells, of the species involved in the reaction. Lewis acids and bases can be classified on this basis as follows: *Hard acids* are Lewis acids which are not easily polarized, i.e. small, highly charged cations and molecules in which a high positive charge is induced on the central atom (e.g. H^+, Li^+, Mg^{2+}, Al^{3+}, Ti^{4+}, Fe^{3+}, CO_2, SO_3). *Soft acids* are Lewis acids which are highly polarizable, e.g. cations with large radius and low charge, or molecules with relatively high-energy occupied molecular orbitals (e.g. Ag^+, Cu^{2+}, Pd^{2+}, Pt^{2+}, carbenes, Br_2, I_2). *Hard bases* are Lewis bases with high electronegativity and thus low polarizability (e.g. NH_3, H_2O, OH^-, OR^-, F^-). *Soft bases* are Lewis bases with low electronegativity and thus higher polarizability (e.g. H^-, CN^-, R_3P, RSH, I^-). The terms hard and soft are relative, and gradual transitions are possible. Pearson found that hard acids react preferentially with hard bases, while soft acids react more readily with soft bases. This principle has been very useful for estimating equilibrium positions and the stability of the products, especially in organic and coordination chemistry. As an example, a complex of hard central ion and hard ligands or of soft central ion and soft ligands is much more stable than a hard-soft combination.

Acid-base disproportionation: see Acid-base concepts, section on Brønsted definition.

Acid-base titration: same as Neutralization analysis (see).

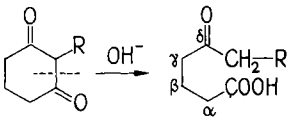
Acid carmoisin B: see Fast red.

Acid cleavage: the cleavage of 1,3-dicarbonyl compounds by heating in alkali solutions. A 1,3-diketone yields a ketone and a carboxylic acid:

$$R\text{–}CO\text{–}CH_2\text{–}CO\text{–}R \xrightarrow{OH^-} R\text{–}CO\text{–}CH_3 + R\text{–}COO^-.$$

Cyclic diketones yield δ-oxocarboxylic acids, and C-alkylated acetoacetates yield acetic acid and a higher carboxylic acid:

$$CH_3\text{–}CO\text{–}CHR\text{–}COOC_2H_5 \xrightarrow{2HO^-} CH_3COO^- + R\text{–}CH_2\text{–}COO^- + 2C_2H_5OH.$$



Acid constant: see Acid-base concepts, section on Brønsted definition.

Acid consumption: see Hardness, 2.

Acid dyes: a group of synthetic dyes which are directly adsorbed to animal fibers (wool, silk); the dye is precipitated on the fiber by addition of sulfuric, acetic or formic acid and sodium sulfate (formation of a water-insoluble "dye acid"). The A. are adsorbed to plant fibers (cotton) only after pretreatment of the fibers (see Mordant dyes). The most important A. are azo dyes, but the group also includes nitro, triphenylmethane, anthraquinone, pyrazolone, quinoline and azine dyes.

Acid halides: 1) derivatives of oxygen acids in which one or more OH groups are replaced by halogen atoms. Some important A. of inorganic oxygen acids are silicon tetrafluoride, SiF_4, sulfuryl chloride, SO_2Cl, thionyl chloride, $SOCl_2$, chlorosulfonic acid, HSO_3Cl, phosgene, $POCl_2$, phosphorus oxygen chloride, $POCl_3$, phosphorus(III) chloride, PCl_3, phosphorus(V) chloride, PCl_5, nitrosyl chloride, NOCl and chromyl chloride, CrO_2Cl_2.

2) ***Acyl halides***, ***carboxylic acid halogenides***: derivatives of carboxylic acids in which the hydroxy group in the carboxyl group is replaced by a halogen atom. The name is constructed either from the names of the skeleton hydrocarbon and the suffix -oyl halide, as in ethanoyl chloride, or by addition of the suffix -carbonyl halide to the name of the root hydrocarbon which is one C-atom shorter, as in methanecarbonyl chloride. Trivial names are also used, e.g. acetyl chloride. Acyl halides are reactive compounds, and they are used as acylating reagents, especially the chlorides. They are usually less water-soluble and have lower boiling or melting points than the parent carboxylic acid. They are made from the carboxylic acid or its salts or anhydride; the acid is reacted with an inorganic A. For example, the

chlorides are made by reaction of the acid, salt or anhydride with thionyl chloride, phosphorus(III) chloride, phosphorus oxygen chloride or phosphorus(V) chloride. Carboxylic acid chlorides can be converted to the bromides or iodides by reaction with hydrogen bromide or iodide. The carboxylic acid fluorides can be made by reaction of the chlorides with KHF_2. Acyl halides are excellent acylation reagents for compounds with active hydrogen atoms. On hydrolysis, they yield carboxylic acids, by an addition-elimination mechanism. Reaction with alcohols and phenols yields carboxylic acid esters; reaction with ammonia or amines yields acyl amides, with hydrazine or substituted hydrazines, hydrazides; with hydroxylamine, hydroxamic acids; with sodium azide, carboxylic acid azides; with sodium salts of carboxylic acids, carboxylic acid anhydrides. Acyl halides are used as the acylation reagents in the Friedel-Crafts acylation. They form ketones on reaction with Grignard compounds. Acyl chlorides can be reduced to aldehydes or primary alcohols (see Rosenmund reduction). The Arndt-Eistert synthesis (see) is a method for lengthening the chain of a carboxylic acid, and starts from the carboxylic acid halogenide. In addition to these reactions of the functional group, acyl halides display the usual reactions for the hydrocarbon part, including halogenation of aliphatic acyl halides. Acetyl and benzoyl chlorides are commonly used acyl halides.

Acidimetry: methods of Neutralization analysis (see) in which acids are used as standard solutions. Occasionally, the term is also used when bases are used as standard solutions.

Acidity: 1) acid strength; see Acid-base concepts, Brönsted definition. ***Acidic compounds***, e.g. acidic hydrocarbons, are those which are able to transfer protons to bases. 2) A measure of the H_3O^+ ion concentration of an aqueous solution (see pH).

Acid precipitation, often called ***acid rain***: precipitation (rain, snow, etc.) which has absorbed acidic or acid-forming pollutants (see Air pollution) in addition to carbon dioxide. Even in areas where the air is pure, the carbon dioxide in precipitation results in pH values as low as 5.6. A. is thus any precipitation in which the pH is lower than 5.5. If alkaline gases and particulates are present, higher concentrations of acidic pollutants are required to reduce the pH of the precipitation below 5.5.

Acid protection: a collective term for Corrosion protection (see) of metals and concrete subjected to corrosive media (not just acids) combined with thermal and mechanical stress. A. is achieved by application of ceramic or organic coatings (see Protective layers), or by massive construction using acid-resistant materials (hard polymers, plastics, ceramics).

A. is applied in the chemical and metal industries (pickling of metals), and to some degree also in coal and nuclear power plants, as well as in the production of cellulose, paper, textiles, synthetic fibers and leather products.

Acid reaction: a reaction, e.g. of a pH indicator, which shows that the pH (see) of an aqueous solution is less than 7 (see Ion product of water).

Acid violet, ***formyl violet***: various types of water-soluble, acid triphenylmethane pigments. They are used to dye paper and paints.

Aconitic acid, ***propene-1,2,3-tricarboxylic acid***: $HOOC\text{-}CH_2\text{-}C(COOH)=CH\text{-}COOH$, an unsaturated, water-soluble, triprotic carboxylic acid which can have either the *Z*- or the *E*-configuration. A. is synthesized by dehydration of citric acid at about 175 °C.

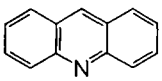
(Z)-A. is a colorless, crystalline compound which is barely soluble in ether; m.p. 130 °C. (*Z*)-A. is an important intermediate in the conversion of citric acid to isocitric acid in the presence of the enzyme aconitase; this is one of the steps of the citric acid cycle. When heated, (*Z*)-A. is readily converted to (*E*)-A.

(E)-A. forms colorless leaflets or needles which are soluble in alcohol; m.p. 198-199 °C. It is found mainly in the form of calcium or magnesium salts in horsetail, sugar cane and grain plants.

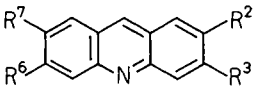
The name A. was coined by Peschier, who first isolated it in 1820 from aconite (*Aconitum napellus*). A. is used in the production of softeners and wetting agents for special purposes.

ACP: abb. for Acyl carrier protein (see).

Acridine, ***dibenzo[b,e]pyridine***, a heterocyclic compound which forms colorless needles with a characteristic odor; m.p. 111 °C (subl.), b.p. 346 °C. A. is nearly insoluble in water, but is soluble in organic solvents and can be steam distilled. The solutions have a blue fluorescence. The tertiary nitrogen atom causes A. to give a basic reaction and to form *acridinium salts* with acids and alkyl and aryl halides. Oxidation of A. with sodium dichromate in acetic acid yields Acridone (see). A. vapors irritate the skin and mucous membranes, and can lead to chronic diseases. A. is a component of coal tar, and can be synthesized by heating diphenylamines with formic acid in the presence of zinc chloride or by zinc powder distillation of acridone. A. is the skeleton of a numbers of dyes (see Acridine dyes) and pharmaceuticals, including antimalarials, bacteriocides and antiseptics. It was discovered in 1870 in coal tar by Graebe and Caro.



Acridine dyes: a group of synthetic dyes based on the acridine skeleton; the auxochromic groups are primary or dialkyl-substituted amino groups. The A. are made by condensation of 2,4-diaminotoluene with formaldehyde or benzaldehyde. The A. are basic mordant dyes used on cotton, leather and silk. The salts of acridine bases alkylated on the ring nitrogen, the acridinium salts, are used as antiseptics and occasionally as antimalarials.

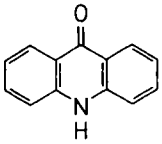


Acridine dye	R^2	R^3	R^6	R^7
Acridine orange	H	$N(CH_3)_2$	$N(CH_3)_2$	H
Acridine yellow	CH_3	$N(CH_3)_2$	$N(CH_3)_2$	CH_3

Some important A. are ***acridine orange***, 3,6-tetramethyldiaminoacridine, and ***acridine yellow***, 3,6-

tetramethyldiamino-2,7-dimethylacridine. The zinc chloride double salt of acridine orange gives a green fluorescence in aqueous solutions; the dye imparts an orange color to cotton.

Acridone: a heterocyclic compound derived from Acridine (see). A. is a stable compound which crystallizes from alcohol in yellow needles; m.p. 354 °C. It is rather insoluble in organic solvents, and displays neither ketonic nor phenolic properties; instead, it exists as an internal salt. Reduction with zinc powder produces acridine. A. is made by ring closure of diphenylamine-2-carboxylic acid (phenylanthranilic acid) with concentrated sulfuric acid, or by oxidation of acridine with sodium dichromate in acetic acid.



Acrilan®: see Synthetic fibers.

Acrolein, ***prop-2-enal, acrylaldehyde***: CH_2=CH-CHO, a colorless, mobile liquid, m.p. - 87.7 °C, b.p. 52.5 °C, n_D^{20} 1.3998. It is a lacrimator and has a pungent odor. A. is soluble in water and most organic solvents. It is the simplest unsaturated Aldehyde (see), and displays all the addition and condensation reactions typical of this class. As an α,β-unsaturated aldehyde with conjugated π-electrons, A. also has unusual reactions with nucleophilic reagents, which attack not only the carbonyl carbon atom, but also the β-C atom. This nucleophilic attack can be understood on the basis of the following canonical resonance formulas: $^+CH_2$-CH=CH-O$^-$ ↔ CH_2=CH-CH=O ↔ CH_2=CH-$^+$CH-O$^-$.

Acrolein is a strong poison which is extremely irritating to the mucous membranes of the respiratory passages and eyes, and can cause bronchitis and bronchopneumonia.

Because of its very high reactivity, A. tends to polymerize. It is easily converted to acrylic acid by oxidizing agents. Partial hydrogenation of A. on a nickel contact produces propionaldehyde; in the presence of copper-cadmium catalysts, allyl alcohol is formed. A. may be produced in the laboratory by heating glycerol with a dehydrating agent to about 200 °C. Industrially, A. is produced either by an aldol reaction of acetaldehyde and formaldehyde in the presence of silica gel or lithium phosphate, or by oxidation of propene or allyl alcohol on a metal oxide catalyst. A. can be used in the Diels-Alder reaction as the dienophile to synthesize formyl-substituted adducts. A. is also used in the synthesis of pharmaceutical products and many organic compounds.

Acrylaldehyde: same as Acrolein (see).

Acrylates: see Acrylic acid.

Acrylic acid, ***propenic acid, vinylcarboxylic acid, ethene carboxylic acid***: CH_2=CH-COOH, the simplest unsaturated monocarboxylic acid. A. is a colorless liquid with a pungent odor; m.p. 13 °C, b.p. 141.6 °C, n_D^{20} 1.4224. It is readily soluble in water and most organic solvents. It can be stored in monomeric form for a long time in the dark, if stabilizers, such as hydroquinone, are present. Under normal conditions, however, it polymerizes very readily to polyacrylic acid. The reactivity of A. is a result of the C=C double bond and the carboxyl group. These can undergo the reactions typical of their classes either singly or simultaneously, including additions to the C=C double bond, and various types of functionalizations of the carboxyl group. The products are substituted propanoic acids, Diels-Alder cyclization products, acrylic acid derivatives and heterocyclic systems. The salts and esters of A. are called *acrylates*. A. can be synthesized by oxidation of acrolein or allyl alcohol, hydrolysis of acrylonitrile, or dehydration of β-hydroxypropionic acid. Industrially, it is more effective to synthesize A. by gas phase oxidation of propene, by addition of water and carbon monoxide to acetylene in the presence of carbonylnickel(IV), or by catalytic ring cleavage of β-propiolactone. A. is used mainly to produce polyacrylic acid, polyacrylic esters and copolymers, and for organic synthesis.

Acrylic fibers: see Polyacrylonitrile fibers.

Acrylics: see Polymethacrylates, Polyacrylates.

Acrylonitrile, ***vinyl cyanide, acrylic nitrile***: CH_2=CH-C≡N, a colorless liquid with a pungent odor; m.p. - 83.5 °C, b.p. 77.5 °C, n_D^{20} 1.3911. A. is slightly soluble in water and readily soluble in most organic solvents. Because both an activated C=C double bond and the nitrile group, -C≡N, are present, A. is extremely reactive. It polymerizes very readily, forming polyacrylonitrile. In the presence of polymerization inhibitors, such as hydroquinone or pyrocatechol, A. can be stored for longer periods. Chemical reactions can occur on both functional groups, either separately or simultaneously. For example, CH-acidic compounds can add to the C=C double bond (Michael addition) to form cyanoethylated derivatives: R-H + CH_2=CH-C≡N → R-CH_2-CH_2-C≡N. A. can be hydrolysed by aqueous mineral acids to acrylamide or acrylic acid:

Acrylonitrile is a strong poison which can enter the body through the lungs or the skin. It also irritates the skin and mucous membranes of the nose and eyes.

A. can be synthesized by addition of hydrocyanic acid to ethyne, or from ethylene oxide and hydrocyanic acid. Industrially, it is produced by ammoniooxidation of propylene:

A. is used mainly for the production of polyacrylonitrile, and also as an intermediate for organic syntheses.

ACTH: see Corticotropin.

Actin: A type of contractile protein found in many cell types. A. is an essential component of the contractile complex of Muscle proteins (see). Microvilli, microspikes (filopodia), and stereocilia (hair cells in the cochlea of the ear and other related organs) consist of A. associated with other proteins. Microfilaments in the cell cytoplasm consist of F- (polymerized) A. Monomeric, or G-A. (M_r 41 720) is an irregular mass, approximately ellipsoidal in shape. A consensus model of F-A. shows a helical filament

with a diameter of 90-100 Å. The monomers lie with their long axes nearly perpendicular to the filament axis. The positions of the monomers within the filament are flexible, so that binding of proteins (e.g. tropomyosin) to the filament may impose a periodic but non-helical structure; the repeat distance is 7 monomers.

The structure of A. has been highly conserved in the course of evolution; this may be due to the large number of proteins with which it interacts specifically. In muscle fibrils, it forms a complex with regulator proteins, of which the best known are ***tropomyosin*** (M_r 68,000) and ***troponin*** (M_r 80,000). These are associated with the protein myosin in the *actomyosin complex*, which is responsible for the contraction of muscle. A. is present in all eukaryotic cells, as part of the *cytoskeleton*, where it makes up the microfilaments, and is involved in cell motions.

Actinium, symbol ***Ac***: a radioactive element from Group IIIb of the periodic system, the Scandium group (see). A. is a heavy metal, atomic number 89. The natural isotopes are members of the ^{235}U and ^{232}Th decay series, and have mass numbers 227 (β-emitter, $t_{1/2}$ 21.772 years) and 228 (β-emitter, $t_{1/2}$ 6.13 h). The atomic mass of Ac is 227.0278, its valence is III, and its density is calculated to be 10.07; m.p. 1050 °C, b.p. 3300 °C, standard electrode potential (Ac/Ac^{3+}) = - 2.6V.

A. is a regular, silvery-white metal forming cubic close-packed crystals; because of its radioactivity, it shines in the dark. Metallic A. is obtained by reduction of actinium(III) fluoride with lithium vapor at 1100 to 1300 °C. The chemistry of A. is very similar to that of lanthanum, its lighter homolog in the scandium group. Ac is very reactive, with surface oxidation occuring in air even at room temperature; in compounds, its valence is always +3. It is found naturally in uranium ores, but because of its short half-life, it is present only in very small concentrations. For example, 1 t pitchblende contains only 0.15 mg Ac. Ac makes up about $6.1 \cdot 10^{-14}$% of the earth's crust. It is produced in gram amounts by neutron irradiation of radium:

$$^{226}_{88}Ra \xrightarrow{+n} {}^{227}_{88}Ra \xrightarrow{-\beta^-} {}^{227}_{89}Ac.$$

In addition to the naturally occurring isotopes, 24 synthetic isotopes with mass numbers from 209 to 226 and 229 to 232 are known; there are two nuclear isomers each with mass numbers 216 and 222.

Historical. A. was discovered in 1899 by André Debierné in pitchblende residues. The name (from the Greek "aktinoeis" = "shining") refers to the radioactivity of the element.

Actinium emanation: see Radon.

Actinoid: one of the 14 radioactive elements following actinium in the periodic system, with atomic numbers 90 to 103: thorium (Th), protactinium (Pa), uranium (U), neptunium (Np), plutonium (Pu), Americium (Am), curium (Cm), berkelium (Bk), californium (Cf), einsteinium (Es), fermium (Fm), mendelevium (Md), nobelium (No), and lawrencium (Lr). They are represented by the common symbol ***An***. A. with atomic numbers 93 to 103, the Transuranium elements (see), can only be obtained by nuclear reactions.

Table 1. Properties of the actinoids

	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cr	Es	Fm	Md	No	Lr
Nuclear charge	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Electron configuration*	$6d^2 7s^2$	$5f^2 6d^1 7s^2$	$5f^3 6d^1 7s^2$	$5f^5 7s^2$	$5f^6 7s^2$	$5f^7 7s^2$	$5f^7 6d^1 7s^2$	$5f^8 6d^1 7s^2$	$5f^{10} 7s^2$	$5f^{11} 7s^2$	$5f^{12} 7s^2$	$5f^{13} 7s^2$	$5f^{14} 7s^2$	$5f^{14} 6d^1 7s^2$
Atomic mass	232.0381	231.0359	238.029	237.0482	244	243	247	247	251	252	257	258	259	260
Atomic radius [pm]	179.8	160.6	139	131	151.3	173.0	174.4	176.7	186	186				
Density [g cm^{-3}]	11.724	15.37	18.97	20.48	19.737	13.671	13.51	13.25						
m.p. [°C]	1755	1568	1132	639	639.5	1173	1350	986	900					

* Electrons outside the Rn shell.

Table 2. Colors of some important actinoid ions

An^{3+}			U^{3+} Red-brown	Np^{3+} Faint purple	Pu^{3+} Blue violet	Am^{3+} Pink	Cm^{3+} Pale Yellow
An^{4+}	Th^{4+} Colorless	Pa^{4+} Yellow-green	U^{4+} Emerald green	Np^{4+} Yellow-green	Pu^{4+} Brown	Am^{4+} Reddish pink	Cm^{4+} Pale Yellow
AnO_2^+		PaO_2^+ Colorless	UO_2^+ Pale lilac	NpO_2^+ Green	PuO_2^+ Pale violet	AmO_2^+ Yellow-brown	
AnO_2^{2+}			UO_2^{2+} Yellow	NpO_2^{2+} Wine red	PuO_2^{2+} Fire red	AmO_2^{2+} Dark yellow	

A. have occupied outer orbitals ($6s^2$, $6p^6$, $7s^2$, and sometimes $6d^n$ where $n = 1$ or 2), and differ with respect to the occupation of the 5f shell.
Chemically, the A. differ more from one another than do the homologous lanthanoid group elements. With the exception of thorium, all A. form An^{3+} ions, the colors of which vary in a characteristic fashion (Table 2).

The absorption spectra of An^{3+} ions have narrow bands which are about ten times more intense than the bands of the corresponding Ln^{3+} ions; they are due to electron transitions within the 5f shell. Other similarities between the A. and lanthanoids are seen in the decrease in ionic radii of the An^{3+} ions with increasing nuclear charge number (see Actinoid contraction), the isomorphism of many actinoid and lanthanoid derivatives, such as the trichlorides, $AnCl_3/LnCl_3$, and dioxides, AnO_2/LnO_2, in the magnetic properties of An^{3+} and Ln^{3+} ions, and in their behavior on ion exchangers.

Thorium, protactinium and uranium have some similarities to the elements of Groups IVb, Vb and VIb. Plutonium, neptunium and americium are especially closely related to uranium, and the heavy A. curium to lawrencium are quite similar to the lanthanoids, with the +3 oxidation state the dominant one (Table 3).

Table 3. Valencies of the actinoids

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
					2			2	2	2	2	2	
	3	3	3	3	3	3	3	3	3	3	3	3	3
4	4	4	4	4	4	4	4	4					
	5	5	5	5	5								
		6	6	6	6								
			7	7	7								

The A. are silvery-white, reactive metals which are tarnished by air and react at elevated temperatures with non-metals such as oxygen, hydrogen, nitrogen, carbon or halogens, to form the corresponding binary compounds (see Actinoid compounds).

Of the A., essentially only thorium, uranium and protactinium are found in nature; plutonium and neptunium are found only in exceedingly small traces. Those which are not found in nature can be made from uranium, or from pure transuranium elements obtainable from uranium, by nuclear reactions. Plutonium (^{239}Pu) and neptunium (^{237}Np) are generated in considerable quantity in nuclear reactors, and can be obtained on industrial scale by working up spent uranium fuel rods. A. with atomic numbers > 100 are obtained by bombardment of lighter A. with α-particles or accelerated carbon or boron nuclei:

$$^{253}_{99}Es + {}^{4}_{2}He \longrightarrow {}^{256}_{101}Md + {}^{1}_{0}n$$

$$^{244}_{96}Cm + {}^{12}_{6}C \longrightarrow {}^{252}_{102}No + 4\,{}^{1}_{0}n$$

$$^{252}_{98}Cf + {}^{11}_{5}B \longrightarrow {}^{257}_{103}Lr + 6\,{}^{1}_{0}n$$

The lighter A. are separated using the considerable differences in stability of their various oxidation states ($UO_2^{2+} > NpO_2^{2+} > PuO_2^{2+} > AmO_2^{2+}$; U^{4+}, Np^{3+};≪ $Pu^{3+} < Am^{3+}$). The heavier A., like the lanthanoids, are separated by ion-exchange chromatography on the basis of the actinoid contraction. The smaller their atomic numbers, the more tightly A^{3+} ions are bound to cation exchangers, while extraction with complex formers, such as citrate, lactate or α-hydroxyisobutyrate, occurs more readily for the heavier An^{3+} ions with smaller ionic radii. Thus the A. ions appear in the eluate in the order Lr^{3+}, No^{3+} ... Bk^{3+}, Cm^{3+}.

Metallic A. can generally be obtained by reduction of the anhydrous fluorides MF_3 or MF_4 with magnesium or lithium-calcium vapor at 1100 to 1400 °C, or by melt electrolysis.

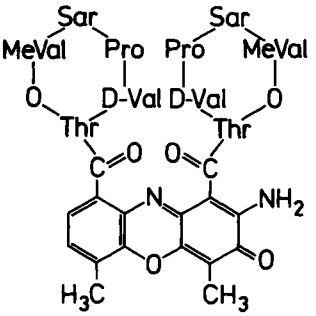
Actinoid compounds: The variety of A. is greater than that of the homologous lanthanoids, due to the ability of actinoids to exist in more oxidation states and to the differing stabilities of these states in different elements. For the elements curium to lawrencium, the +3 state is most important; the chemistry of thorium is dominated by the +4 state, which also is important for americium and plutonium. Protactinium and neptunium prefer the +5 state, while the +6 state is typical for uranium. With regard to the number of possible oxidation states, neptunium, plutonium and americium (+3 to +7) are comparable to uranium (+3 to +6), and these four elements tend to form dioxometal(VI) cations, AnO_2^{2+}, in aqueous solutions. The +2 oxidation state is limited to americium, as eka-europium, and the heavier actinoids californium to lawrencium. Actinoids form binary compounds with nonmetals such as hydrogen, carbon, fluorine and chlorine, including hydrides with the general formula AnH_3 (An = Pa, U, Np, Pu and Am), carbides AnC (cubic, NaCl-type crystals), An_2C_3 and AnC_2, and halides AnX_3 and AnX_4. The trichlorides, $AnCl_3$, of uranium to curium have ninefold coordination; while those of californium and einsteinium are dimorphic. The trifluorides AnF_3 of uranium to curium are isomorphic with the lanth-

anoid(III) fluorides, and also form polyhedra with a coordination number of 9. The trifluorides of berkelium and californium are dimorphic. The tetrafluorides AnF_4 are generally characterized by 8-fold coordination (distorted antiprisms). An^{3+} and An^{4+} ions, like the lanthanoid ions Ln^{3+}, can be precipitated by addition of fluoride or oxalate as hydrated actinoid(III) or (IV) fluorides or oxalates. Actinoid(IV) oxides, AnO_2, which crystallize in fluorite lattices, are known for An = thorium to californium; octahedral actinoid(VI) fluorides, AnF_6, have been obtained for An = uranium, neptunium and plutonium. The +5 and +6 valence states are represented by dioxoactinoid(V) and dioxoactinoid(VI) cations, which have been reported for protactinium to americium (AnO_2^+) and uranium to americium (AnO_2^{2+}), respectively. Actinoid(VII) derivatives are represented by lithium perneptunates and perplutonates of the type Li_5AnO_6 (An = Np, Pu).

Actinoid contraction: the continuous decrease in ionic radii with increasing nuclear charge among the actinoids: U^{3+}, 102.5 pm; Np^{3+}, 101.2 pm; Pu^{3+}, 100 pm; Am^{3+}, 97.5 pm; Cm^{3+}, 96.0 pm; Bk^{3+}, 95.5 pm; Cf^{3+}, 94.2 pm; Es^{3+}, 92.8 pm. Like the Lanthanoid contraction (see), the A. is caused by incomplete shielding of the increasing nuclear charge by the 5f electrons.

Actinometer: a device to determine the number of photons in a beam of ultraviolet or visible light, either as a time integral or per unit of time. Such information is needed to determine the quantum yields of photochemical reactions and photophysical processes. Bolometers and photodiodes are examples of physical A. In chemical A., the amount of radiation is determined by the amount of substance undergoing a photochemical reaction of known quantum yield. There are different A. for the various wave-length ranges. The ***ferrioxalate A.*** is very frequently used; it is based on the decomposition of $K_3[Fe(C_2O_4)_3]^{3-}$ into Fe^{2+} and oxalate ions and carbon dioxide. This reaction is useful because of its high quantum yield (1.25 to 0.9, depending on the wavelength), its wide range (250 to 480 nm) and the ease of measuring the concentration of the products (calorimetric determination of Fe^{2+} as the o-phenanthroline complex).

Actinomycins: a large group of peptide lactone antibiotics produced by various strains of *Streptomyces*. These highly toxic red compounds contain a chromophore, 2-amino-4,6-dimethyl-3-ketophenoxazine-1,9-dioic acid (actinocin), which is linked to two 5-membered peptide lactones by the amino groups of two threonine residues. The various A. differ only in the amino acid sequence of the lactone rings. In vivo, A. inhibit DNA-dependent RNA synthesis at the level of transcription by interacting with the DNA. The concentration required for inhibition depends on the base composition of the DNA; more is required for DNA with a low guanine content. A. are pharmacologically very important due to their bacteriostatic and cytostatic effect. Actinomycin D (Fig.) is one of the most widely occurring A. Its spatial structure has been elucidated by NMR studies, and the specificity of its interaction with deoxyguanosine was demonstrated by X-ray analysis. Actinomycin D is used as a cytostatic, e.g. in the treatment of Hodgkin's disease.



Actinomycin D

Actinon: see Radon.

Action constant: see Arrhenius equation.

Activated acetic acid: see Coenzyme A.

Activated complex: see Kinetics of reaction (theory).

Activated sludge: see Sewage treatment.

Activation analysis: a physical method of quantitative analysis based on the reaction of atomic nuclei with neutrons or charged particles, leading to formation of a radioactive isotope of the element to be analysed. The reaction utilized in neutron A. can be described by the following equations: 1) formation of the radioactive isotope:

$$^{A}_{Z}X + {}^{1}_{0}n \longrightarrow {}^{A+1}_{Z}X + \gamma$$

2) Decay of the isotope:

$$^{A+1}_{Z}X \longrightarrow {}^{A}_{Z+1}Y + \beta^-$$

The amount of radioactive isotope formed depends on the neutron flux, the number of reactive nuclei in the sample, and the capture cross section σ of these nuclei. σ is a measure of the probability of reaction 1), and is inversely proportional to the energy of the neutrons. Therefore A. is usually done with slow neutrons, which are present in high flux densities in nuclear reactors.

In practice, the unknown sample is usually irradiated along with a comparison sample of known composition, under identical conditions, and the activities generated after a sufficient time are compared. The simple equation $G_x/G_c = n_x/n_c$ is applied; here G_x is the amount of the substance being determined in the unknown sample, G_c is the amount in the comparison sample, n_x is the count rate of the unknown sample and n_c is the count rate of the comparison.

A. is a very sensitive method used mainly in Trace analysis (see), since the β-radiation emitted according to eq. 2) is readily measured. Some disadvantages are the very long time required for activation, and the fact that the process must be done in a nuclear reactor.

Activation energy: see Arrhenius equation.

Activation enthalpy: see Kinetics of reactions (theory).

Activation entropy: see Kinetics of reactions (theory).

Activator: see Catalysis, sect. III; Trace elements, 2.

Activity: 1) in solution theory, the corrected mass number for the composition of real solutions. The most common measures of Concentration (see) are mole fractions x_i, concentrations c_i and molalities m_i. In an ideal solution, the sum of the molecular interactions between the components is the same as in the pure substances. In real solutions, additional interaction energies appear, and lead to deviations in all the laws of solutions which were originally derived on the assumption of ideal behavior (e.g. the mass action law, the Nernst equation or the solubility product). In order to retain the equations for ideal solutions, Lewis introduced a corrected composition variable, the A. a, which is the product of the concentration and the ***activity coefficient*** f: $a_x = f_x x$; $a_c = f_c c$; $a_m = f_m m$.

The definition of A. is based on the chemical potential μ_i: $\mu_{real} = \mu_{ideal} + \Delta\mu_i = \mu_i^\circ + RT \ln x_i + \Delta\mu_i$. Here μ_i° is the standard chemical potential of substance i, x_i is the mole fraction of substance i in the solution, and $\Delta\mu_i$ is the difference between the chemical potential in the real solution and an ideal solution. $\Delta\mu_i$ corresponds to the reversible molar work of transferring substance i from the ideal into the real solution. According to Lewis, $\Delta\mu_i$ is set equal to $RT \ln f_i$; it follows that $\mu_{real} = \mu_i^\circ + RT \ln x_i + RT \ln f_{x,i}$ and $\mu_{real} = \mu_i^\circ + RT \ln a_{x,i}$ where $a_{x,i} = f_{x,i} x_i$. The mole fraction times the correction factor is the A., $a_{x,i}$, and the correction factor $f_{x,i}$ is the activity coefficient.

For practical purposes, chemical potentials can be formulated with concentrations c_i or molalities m_i and corresponding standard potentials μ_i°. Deviations from ideal behavior require the definition of A. as $a_{c,i} = c_i f_{c,i}$ or $a_{m,i} = m_i f_{m,i}$. The subscripts c and m indicate that the A. are corrected concentrations and molalities, respectively. The numerical values of the activity coefficients defined in these three ways are not the same.

Activity coefficients depend on concentration, because the additional interactions vary with the composition of the solution. In the ideal solution, the activity coefficients are equal to 1. The ideal solution is defined in different ways. For mole fraction activities $a_{x,i}$, it is usually the pure substance, i.e. $f_{x,i} = 1$ for $x_i = 1$. For concentration and molality A., the ideal solution is an infinitely dilute one, i.e. $f_{x,i} = 1$ for $c_i \to 0$ and $f_{m,i} = 1$ for $m_i \to 0$.

Although solutions of neutral molecules have nearly ideal behavior at low concentrations, and the mass action or Raoult laws (for example) can be approximately formulated with concentrations instead of activities, in electrolyte solutions the long-range electrostatic interactions of the ions produce large deviations from ideal behavior even at concentrations $< 10^{-3}$.

Activity coefficients must be determined experimentally. For dilute solutions of strong electrolytes, they can be calculated using the Debye-Hückel theory (see).

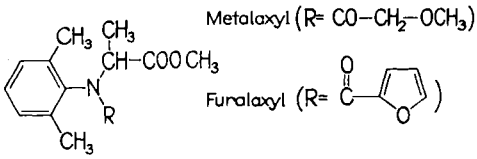
2) See Optical activity.

Activity coefficient: see Activity.

Acyclic: a term for organic compounds in which the carbon atoms are arranged in a chain, especially in contrast to cyclic compounds.

Acyl ...: a term for the atomic group R-CO- in a molecule, for the unstable radical R-CO· and for the cation $R\text{-}CO^+$.

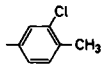
Acylalanine fungicide: a systemic Fungicide (see) containing an acylated phenylalanine component. The substances effective against oomycetes specifically inhibit RNA synthesis. *Metalaxyl* (Ridomil®), which is effective in low concentrations against *Phytophthora, Pythium* and *Peronospora*, is used on potatoes to prevent tuber and leaf rot. It is usually combined with other fungicides to prevent development of resistance. A. is synthesized by reaction of dimethylaniline with 2-bromopropionic acid methyl ether; the product is then acylated to methoxyacetyl chloride. *Furalaxyl* is used on ornamentals.



Acylals: organic compounds of the type $R^1R^2C(O\text{-}CO\text{-}R^3)_2$; they are esters of geminal diols with carboxylic acids. A. are formed, for example, by oxidation of methylarenes with chromic acid in acetic anhydride. They prevent further oxidation to the carboxylic acid, and thus give access to formyl arenes, which are readily obtained by hydrolysis of the isolated A.

Acylaniline herbicides: Herbicides (see) which contain an anilide structure.

Table 1. Anilide herbicides $R\text{–}C(=O)\text{–}NH\text{–}Ar$

Name	R	Ar
Propanil	C_2H_5	
Pentanochlor		
Monalid		
Chloranocryl		

1) Anilides derived from low-molecular-weight carboxylic acids (Table 1) act as photosynthesis inhibitors; in most cases they are applied as post-emergence, selective contact herbicides.

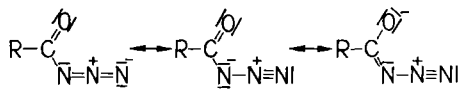
2) Chloroacetanilide herbicides, i.e. derivatives of chloroacetic acid (Table 2) usually inhibit protein synthesis. They are usually used as pre-emergence herbicides which are highly effective against grasses.

Table 2. Chloroacetanilide herbicides 

Name	R	Ar
Propachlor	$(H_3C)_2CH$	
Prynachlor		
Alachlor	H_3COCH_2	
Butachlor	$H_9C_4OCH_2$	

Acylation: a preparative method for introduction of an acyl group, R-CO-, into an organic compound. It is usually the H atom of a hydroxyl group (*O-acylation*), sulfhydryl group (*S-acylation*), amino group (*N-acylation*) or arene or alkene (*C-acylation*) which is replaced by the acyl group. The most important acylation reagents are the halides, anhydrides and esters of carboxylic acids. O-, S- and N-acylation is frequently used to protect OH, SH and NH_2 groups from undesired side reactions; the acyl group can later be removed easily by hydrolysis. The products of O-, S- or N- acylation are esters, thioesters or amides. These compounds often crystallize well, and are therefore used to characterize alcohols, phenols, thiols and amines. An important A. method for preparative and analytical purposes is the Schotten-Baumann reaction (see) with benzoyl chloride. C-acylation of arenes by the Friedel-Crafts reaction (see) produces aromatic-aliphatic or pure aromatic ketones. The Vilsmeier-Haack reaction on arenes (see) is another A. A further application of A. is the determination of the number of OH, SH or NH_2 groups in an organic compound, the acyl number.

Acyl azides: derivatives of carboxylic acids with the general formula R-CO-N_3. The electronic structure can be described by canonical resonance structures:



C. are obtained by reaction of carboxylic acid chlorides with NaN_3, or by reaction of nitrous acid with carboxylic acid hydrazides. They are very reactive, and the smaller molecules tend to decompose explosively. When heated in a solvent, they undergo Curtius decomposition (see). In inert solvents (benzene, chloroform), isocyanates can be isolated. C. are important acylating reagents. N-Protected amino acids or peptide azides are very important in Peptide synthesis (see).

Acyl carrier protein, abb. ***ACP***: a globular protein with relative molecular mass up to 16,000. The A. is the carrier of the fatty acid chains produced in fatty-acid biosynthesis. They are part of a multienzyme complex, fatty acid synthetase. A serine residue on the ACP is linked to phosphopantetheine, which acts as the "swinging arm" and moves the acyl group from one active site to the next within the complex. The fatty acid is esterified to the thiol group of the phosphopantetheine.

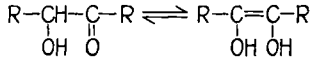
Acyl halides: see Acid halides, 2.

Acyl hydrazines: see Hydrazides.

N-Acylneuraminic acid: same as Sialic acid (see).

Acyl number: the number of acyl groups in a substance. The A. is determined by hydrolysis in alcoholic potassium hydroxide and neutralization of the released acid. For example, 1 ml of a 0.5 M potassium hydroxide solution corresponds to 21.52 mg acetyl or 52.51 mg benzoyl.

Acyloin: a general term for an α-hydroxyketone, R-CH(OH)-CO-R. The R groups can be alkyl, aryl or heterocyclic substituents; mixed A. are also known. A. are in tautomeric equilibrium with enediols, and are therefore capable of reducing Fehling's solution.

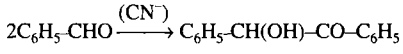


Aliphatic A. are formed when carboxylate esters are heated with sodium in inert solvents, in the absence of water, oxygen and alcohols. Cyclic A. are formed from dicarboxylic acid esters. Aromatic and heterocyclic A. are formed mainly through Acyloin condensation (see). Some important A. are Acetoin (see), Benzoin (see) and Furoin (see).

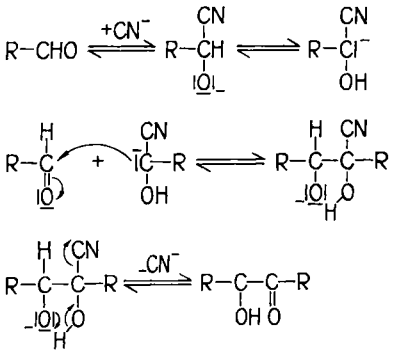
Acyloin addition: same as Acyloin condensation.

Acyloin condensation, ***acyloin addition***: 1) a dimerization of aromatic or heterocyclic aldehydes which do not have α-hydrogen atoms to form acyloins.

The classic example of A. is the ***benzoin condensation***, in which benzaldehyde forms benzoin in the presence of potassium cyanide or special thiazolium or imidazolium salts in a water/alcohol solution:



The following reaction mechanism is considered definitive:



Anisaldehyde and furfural, for example, react in the same way to form symmetric, substituted α-hydroxyketones, anisoin and furoin. A number of unsymmetric benzoins can also be synthesized under the conditions of the A. For example, a mixture of benzaldehyde and 4-dimethylaminobenzaldehyde in the presence of cyanide ions yields a benzoin with the following structure: $(CH_3)_2N\text{-}C_6H_4\text{-}CO\text{-}CH(OH)\text{-}C_6H_5$.

2) The formation of acyloins from aliphatic carboxylic acid esters and sodium in inert solvents.

N-Acylsphingoid: same as Ceramide (see).

"Adam and Eve" cycle: see Synthesis gas.

Adamantane, ***tricyclo[3.3.1.1^{3,7}]decane***: a saturated hydrocarbon forming colorless crystals with a camphor-like smell. It sublimes at room temperature; m.p. 270 °C. A. is found in petroleum and was first isolated from that source.

Adamantane

It is synthesized by isomerization of *endo*-tetrahydrodicyclopentadiene by aluminum chloride. A. is the parent compound of the "diamond-like" compounds. 10 carbon atoms are linked to form four completely equivalent, non-stressed cyclohexane rings which are fixed in the chair form. The highly symmetrical structure is an optimal arrangement and approximates a sphere (it is also similar to Urotopin). A. is therefore very stable and unreactive. It is impossible for steric reasons to form a double bond, i.e. Bredt's rule applies strictly to each C atom.

Adamsite: see Chemical weapons.

Addition: incorporation of atoms or molecules into unsaturated organic compounds. In the process, triple bonds are converted to double bonds, and double bonds, to single bonds. If cyclic compounds are formed by A., one speaks of Cycloaddition reactions (see). A. can occur as Electrophilic reactions (see) (A_E), Nucleophilic reactions (see) (A_N) or Radical reactions (see) (A_R). The A. of hydrogen is called Hydrogenation (see); A. of water is called Hydration (see). A. reactions are catalysed by acids. A. of bases to special carbonyl compounds with cumulative double bonds are important in the synthesis of carboxyl derivatives, for example A. to carbon dioxide to form carboxylic acid derivatives, A. to carbon disulfide to form xanthogenates, A. to mustard oils and isocyanic acid or its esters to form urea derivatives and urethanes, or A. to ketenes to form acetic acid derivatives. The reactions of carbonyl compounds with CH-acidic compounds are also A. in which the anion of the CH acidic compound is added to the carbonyl carbon atom by a nucleophilic mechanism. Seen in this way, the reaction of carbonyl compounds with certain bases occurs by an addition-elimination mechanism (see Substitution 1.3.2). A. can also be assumed to be steps in the nucleophilic substitutions of benzene derivatives, which occur by addition-elimination or elimination-addition mechanisms.

Addition complex: see Coordination chemistry.

Addition-elimination mechanism: see Substitution 1.3.2.

Additives: chemical substances added in small amounts to materials to achieve a desired effect or diminish undesired properties.

1) In the petroluem industry, the most notorious is tetraethyllead, $Pb(C_2H_5)_4$, which increases the octane rating of gasolines.

a) *Antioxidants* suppress autooxidation of lubricants; 2,6-di-*tert.*-butyl-p-cresol is widely used for this purpose.

b) *DD additives* (detergents-dispersants) are intended to prevent formation of deposits in combustion engines. Insoluble tars and solids which form in the lubricating oil or are picked up by it are kept in fine suspension and prevented from forming a sludge in the engine. Salts of alkylarylsulfonic acids are used for this purpose.

c) *HD additives* (heavy-duty A.) have a function similar to that of the DD-A., but they are used in more heavily stressed engines, particularly those burning sulfur-containing diesel fuels.

d) *Stock-point lowering A.* prevent formation of paraffin crystals in lubricating oils at low temperatures. If such crystals form, the oil components are adsorbed on them, causing the entire oil to solidify prematurely. Low-molecular-weight ethylene-vinyl acetate copolymers and highly alkylated naphthalene derivatives made from chloroalkanes and naphthalene are used for this purpose.

e) *Viscosity-temperature A.* are used to counteract the decrease in viscosity of lubricants at higher temperatures. These compounds are high polymers, such as polyisobutylene, copolymers of styrene with C_8 to C_{12} alkenes, and polymethacrylates with molecular weights between 10,000 and 30,000.

f) *EP additives* (extreme-pressure A.) are added to gear oils. They usually have high contents of sulfur or phosphorus. When they are used in heavily loaded gears, a sulfide or phosphide film forms on the metal surfaces and prevents binding.

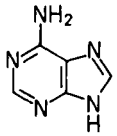
2) In the food industry, A. are substances deliberately added to foods and ingested by the consumers. A. are intended to improve the appearance, consistency and flavor of the product or prolong its shelf life. A. are subject to regulations concerning their effects on health; they must be harmless and must not lead to formation of harmful substances in the foods. Some examples of A. are Food colorings (see), Flavorings (see), Antioxidants (see), Preservatives (see), sweeteners, acidifiers, leavenings and emulsifiers (see Emulsion).

Additivity principle: It is possible to calculate a number of molecular properties to a good approximation from the contributions (increments) of atoms, atomic groups and individual bonds in the molecule. The atomization energy E_A of a molecule can be determined by addition of mean Bond energies (see) E_B(X-Y). As an example, for methanol one obtains $E_A(CH_3OH) = 3\,E_B(C\text{-}H) + E_B(O\text{-}H) + E_B(C\text{-}O)$. In more exact increment systems, the hybridization states of the atoms involved in the bonds must be taken into consideration. The dipole moment of a molecule can be calculated by vectorial addition of bond dipole moments or group moments: $\mu(H_2O) = 2\,\mu_{O\text{-}H}\cos(HOH/2)$. The molar refraction (see Polari-

zation) is the sum of the atomic refractions R_A with special increments for multiple bonds: $R(C_2H_5OH) = 6\ R_H + 2\ R_C + R_O$. Alternatively, it can be obtained from the bonding reactions $R_{X\text{-}Y}$: $R(H_3C\text{-}CH_2\text{-}OH) = 5\ R_{C\text{-}H} + R_{C\text{-}C} + R_{C\text{-}O} + R_{O\text{-}H}$. Conjugated multiple bonds increase the molar refraction (*exaltation*). The A. arises from the fact that the electron density of many molecules can be adequately described by bonding orbitals.

Ade: abb. for Adenine.

Adenine, ***6-aminopurine*** abb. ***Ade***: a component of adenosine and its nucleotides, of RNA and DNA, and of coenzymes such as NAD(P) and FAD. A. crystallizes with 3 mol water; at 110 °C it loses this water of crystallization. It sublimes around 200 °C. It is nearly insoluble in cold water, but readily soluble in mineral acids or alkali hydroxides, with which it forms salts. It is practically insoluble in ether and chloroform. A. derivatives have cytokinin activity. A. is degraded in the human body to uric acid. It is used to treat liver disease. ***Adenine sulfate*** prolongs the storage life of erythrocytes and is used in blood-stabilizing solutions.



Adenosine, ***6-aminopurine-9-β-D-ribofuranoside***, abb. ***Ado***: a purine nucleoside. It crystallizes with 1.5 mol water of crystallization. A. is a white powder, m.p. 229 °C (dec.), $[\alpha]_D^{20}$ - 60° (water), which is soluble in hot water, but practically insoluble in ethanol. It can be isolated from yeast nucleic acid after alkaline hydrolysis. A. has a weak dialtory effect on blood vessels.

Adenosine 5'-diphosphate: see Adenosine phosphates.

Adenosine monophosphates: see Adenosine phosphates.

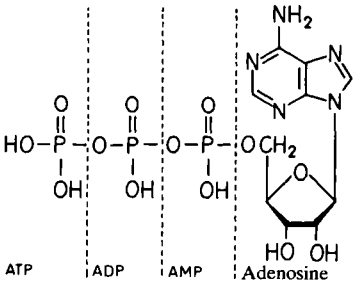
Adenosine 3',5'-phosphate: see Cyclic nucleotides.

Adenosine 3-phosphate-5'-phosphosulfate: see Nucleotides.

Adenosine phosphates, ***adenylic acids***: nucleotides of adenosine. ***Adenosine 5'-monophosphate***, abb. ***AMP*** (***muscle adenylic acid***) is a white, crystalline powder; M_r 347.2, m.p. about 196 °C (dec.). It is soluble in hot water, and slightly soluble in ethanol. ***Adenosine 3'-monophosphate*** (***yeast adenylic acid***) forms white crystalline needles; m.p. 208 °C (dec.). It is soluble in hot water. ***Adenosine 5'-diphosphate***, abb. ***ADP***, M_r 427.2. ***Adenosine 5'-triphosphate***, abb. ***ATP***, M_r 507.2. In pure form, ATP is a white powder which is readily destroyed by acids or bases; however, as the dibarium salt, it precipitates readily in anhydrous form and is relatively stable. ATP is readily soluble in hot water; it forms insoluble salts with barium, lead, silver and mercury.

AMP, ADP and ATP form a metabolic system which is essential to life. It connects the energy-producing processes (photosynthesis, respiration and glycolysis) with energy-consuming synthetic processes. ATP is the most important intracellular energy transferring compound. When hydrolysed to ADP, it releases 32.66 kJ mol^{-1} energy.

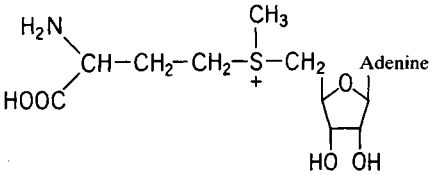
ATP is synthesized in the course of energy-producing reactions by phosphorylation of ADP. In addition to their roles in intermediary metabolism, ATP-cleaving enzymes (ATPases) are active in the transport of various compounds and ions across biological membranes and in the contraction of actomyosin complexes, which power muscle contractions and also motility of non-muscle cells. ATP was first isolated by Lohmann in 1929. ADP and ATP have a dilatory effect, especially on coronary arteries; AMP and adenosine have a similar, but weaker effect. ATP can be isolated as the barium salt from meat extracts.



Adenosine 5'-triphosphate: see Adenosine phosphates.

Adenosine triphosphatases: see ATPases.

S-Adenosylmethionine, abb. ***AdoMet***, a coenzyme of many enzymes which transfer methyl groups (methyl transferases).



Adenylate cyclase system: see Hormones.

Adenylic acids: same as Adenosine phosphates (see).

Adenylic acid system: see Adenosine phosphates.

Adermine: same as Vitamin B_6 (see).

ADH: see Vasopressin.

Adhesion: the sticking together of molecules and particles, or of particles or extended phases of different materials. A. is caused by electric attraction between the particles, due to permanent or induced dipoles (Debye-Keesom forces) or to dispersive forces (London forces, van der Waals forces). ***Adhesive forces*** play a part in adsorption, wetting of solids by liquids, gluing, adhesion of paints, coating of paper, textiles and metals, in the production of filled polymers, in construction materials and in pressure processes. For optimum A., both the properties of the substances and the number of atomic (or molecular) contact sites are important. If the surface is rough or very rigid, glues or higher temperatures are used to promote A.

Adiabat: a curve in a diagram joining all the points through which an adiabatic process passes. If this change in state is also reversible, the A. is also an ***Isentrope***.

Adiabatic: 1) in thermodynamics, a process which occurs without exchange of heat with the environment; see Adiabatic process. 2) In kinetics, a reaction which occurs without any changes in the electronic states of the reactants. The reaction can be described as motion along a potential surface. For thermal reactions at relatively low temperatures, this is the potential surface of the electronic ground state. Non-adiabatic reactions are characterized by a change in the total electron spin, that is, by a transition between two potential surfaces. They occur when the potential surfaces intersect, or at least come very close together.

Adiabatic process: a thermodynamic process which occurs without exchange of heat with the environment, that is, $dq = 0$ (q = heat). An A. is an ideal, limiting case which can only be approximated in practice, for example, by very efficient thermal insulation, or by a reaction which is so rapid that heat transport can be neglected (adiabatic compression and expansion in sound waves or detonation fronts). The opposite ideal case, in which the heat exchange with the environment is so rapid that thermal equilibrium is always maintained, is the ***isothermal process***. Between the two limiting cases lies the region of Polytropic processes (see). From the First Law of Thermodynamics, it follows that since $dq = 0$, $de = dw$, that is, the change in internal energy e of a system is equal to the work exchanged with the environment. When work is done by the system (expansion), it cools, and when work is done on the system (compression), it is heated. For an ideal gas (see State, equation of, 1.1), it follows that $c_v dT = -pdv = -(NRT/v)dv$. Bringing in the equations $c_p - c_v = nR$ and $c_p/c_v = \delta$, we obtain the differential equation $d \ln T = (1 - \varkappa) d \ln v$. The solution of the equation, $Tv^{\varkappa - 1} = \text{const.}$ or $pv^{\varkappa} = \text{const.}$ is called the ***Poisson equation***. Here c_p and c_v are the heat capacities at constant pressure and constant volume, respectively. It follows from the Poisson equation that the pressure of an ideal gas increases more rapidly during adiabatic compression than during isothermal compression, because $\varkappa > 1$ for all gases (see Molar heats).

Adipic acid, *hexanedioic acid, butane-1,4-dicarboxylic acid*: $HOOC-(CH_2)_4-COOH$, a saturated, aliphatic dicarboxylic acid. A. crystallizes in colorless and odorless, monoclinic prisms; m.p. 153 °C, b.p. 265 °C at 13.3 kPa. It is slightly soluble in cold water, and more readily soluble in alcohol and hot water. A. is a stable compound which can be converted to cyclopentanone at high temperatures by loss of carbon dioxide and water. Like all dicarboxylic acids, A. forms mono- and diesters with alcohols. It is found in free form in the juice of sugar beets. It can be prepared by a malonic ester synthesis from sodium malonic esters and 1,2-dibromoethane. Industrially, A. is made by oxidation of cyclohexanone or cyclohexanol with dilute nitric acid or atmospheric oxygen in the presence of a catalyst. A. is synthesized in large quantities as a raw material for production of polyamides and polyesters. It is also used for synthesis of adipic nitrile, softeners and perfumes.

Adipiodone: same as iodipamide; see X-ray contrast agents.

Adiuretin: same as Vasopressin (see).

Ado: abb. for Adenosine (see).

AdoMet: abb. for *S*-Adenosylmethionine (see).

ADP: see Adenosine phosphates.

Adrenalin: see Noradrenalin.

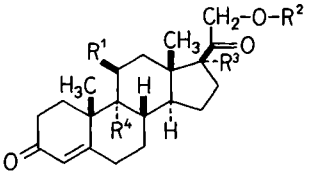
Adrenergics: see Sympathicomimetics.

Adrenal corticosteroids: a group of steroid hormones formed in the adrenal cortex in response to adrenocorticotropic hormone (ACTH). The natural N. are derived from pregnane, and therefore contain 21 C atoms. Oxygen functions are present on C3 and C20; unlike the gestagens, the A. also have oxygen functions on C21 and/or C11 and C17. Over 30 steroids have been isolated from the adrenal cortex, but only a few of them have hormone activity. The biological precursor of the A. is ***progesterone***.

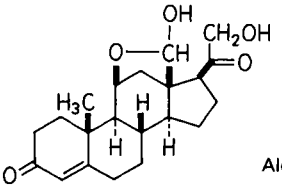
The A. regulate mineral and carbohydrate metabolism. The ***mineralocorticoids*** regulate the plasma concentrations of sodium and potassium ions, causing increased potassium excretion and retention of sodium and water. The first natural mineralocorticoid isolated was *cortexolone*, 17α,21-dihydroxy-4-pregnene-3,20-dione, prepared in 1937 by Reichstein. Its m.p. is 205 °C, $[\alpha]_D^{20}$ + 132° (in ethanol). *Deoxycorticosterone* (cortexone), 21-hydroxy-4-pregnene-3,20-dione, m.p. 142 °C, $[\alpha]_D^{20}$ + 178° (in ethanol), was the first mineralocorticoid used (in the form of its acetate, deoxycorticosterone acetate) for treatment of Addison's disease and shock. The compound was first partially synthesized by Reichstein and Steiger before it was isolated from the adrenal cortex in 1938. *Aldosterone* has about 30 times the mineralocorticoid potency of deoxycorticosterone; in this compound, the C18 is oxidized to a formyl group which forms a semiacetal with the β-OH group on C11. Since aldosterone is poorly absorbed and has an elimination half-life of only 30 minutes, the partially synthetic *fludrocortisone* is used instead, sometimes in the form of its C21 acetate. Fludrocortisone has a somewhat higher glucocorticoid effect than aldosterone, and a much higher mineralocorticoid effect.

Glucocorticoids promote the breakdown of proteins to make amino acids available for gluconeogenesis; this elevates the blood sugar level and leads to glycogen synthesis in the liver. These hormones are also used therapeutically in cases of adrenal insufficiency. However, they are therapeutically more important because of their anti-inflammatory, anti-allergenic, anti-exsudative and immunosuppressive effects. Glucocorticoids are used to treat rheumatism, asthma and various skin conditions. Although a mineralocorticoid effect is desirable for substitution therapy, this effect is undesirable in glucocorticoids for broad use as anti-inflammatory agents, and it has been possible to eliminate it by partial synthetic modification. The most important naturally occurring glucocorticoids are cortisone and hydroxycortisone (*cortisol*), both of which have considerable mineralocorticoid activity. *Cortisone*, 17α,21-dihydroxy-4-pregnene-3,11,20-trione, m.p. 215 °C, $[\alpha]_D^{20}$ +209° (in ethanol) has a weaker glucocorticoid effect than *hydrocortisone*, 11β,17α,21-trihydroxy-4-pregnene-3,20-dione, m.p. 220 °C, $[\alpha]_D^{20}$ +167° (in ethanol).

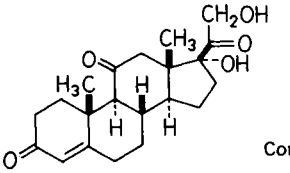
An important advance in the development of compounds with specific glucocorticoid effects was made by the introduction of *prednisone* and *prednisolone*. The glucocorticoid effect of these is 5 times greater than that of hydroxycortisone, while their mineralocorticoid effect is 3 times lower. An improvement in the anti-inflammatory effect and simultaneous elimination of mineralocorticoid activity was achieved by introduction of a fluorine atom in the 9α-position, and introduction of a methyl or hydroxy group on C16. Some examples are *triamcinolone* and *dexamethasone*, which are applied systemically and topically. For topical application only, highly lipophilic compounds are needed which penetrate the skin easily but have no systemic effects. Esters and ketals such as *flumethasone pivalate* and *fluocinolone acetonide* have proven useful in this context.



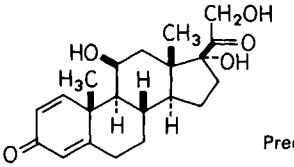
Name	R^1	R^2	R^3	R^4
Cortexolone	H	H	OH	H
Deoxycortone	H	H	H	H
Deoxycortone acetate	H	CH_3CO	H	H
Fludrocortisone acetate	OH	CH_3CO	OH	F



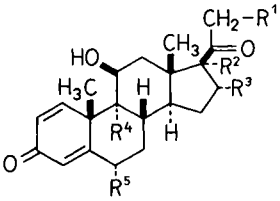
Aldosterone



Cortisone



Prednisolone



Name	R^1	R^2	R^3	R^4	R^5
Prednisolone	OH	OH	H	H	
Triameinolone	OH	OH	OH	F	H
Dexamethasone	OH	OH	CH_3	F	H
Fluocinolone acetonide	OH	-O-C(CH_3)$_2$-O-		F	F
Flumethasone pivalate	(CH_3)$_3$C-COO-OH		CH_3	F	F

Adrenocorticotropin: same as Corticotropin (see).

Adrenolytics: see Sympathicolytics.

Adriamycin: see Anthracyclins.

Adsorbate: term for a system consisting of an adsorbed substance and an adsorbent.

Adsorbent: a condensed phase on the surface of which adsorption occurs. The most commonly used A. are activated charcoal, silica gel, aluminum oxide, zeolite, ion exchangers or polyamides.

Adsorber: an apparatus for carrying out adsorption and desorption, such as a column.

Adsorpt: a substance adsorbed to the surface of a condensed phase.

Adsorption: the enrichment of a substance at the surface of a condensed phase. The process: adsorbed substance + adsorbent ⇌ adsorbate can be treated in the same way as a chemical reaction. The heat released by the process is called ***adsorption energy*** (at constant volume) or ***adsorption enthalpy*** (at constant pressure). Depending on the magnitude of the molar adsorption enthalpy, a distinction is made between reversible ***physical A.*** (physisorption) and irreversible ***chemical A.*** (chemisorption). The former can be reversed by desorption, without chemical change of the adsorbed substance or adsorbent, while the latter cannot. However, a sharp distinction cannot be made. Physical A. is due mainly to van der Waals forces between the adsorpt and adsorbent, and the molar adsorption enthalpies $\Delta_A H$ are between - 5 and - 40 kJ mol^{-1}. In chemical A., chemical bonds form on the surfaces, and $\Delta_A H$ are on the order of - 40 to - 400 kJ mol^{-1}. The surfaces of real solids are not energetically or structurally homogeneous. At the beginning of an A., particles are adsorbed to energetically favored sites, with the result that the enthalpy of A. depends on the amount of substance adsorbed. Heats of A. measured when the amount of adsorbed substance are equal are called ***isosteric heats of adsorption***.

The amount of a substance i adsorbed to a surface is indicated by the surface concentration $\Gamma_i = n_i/S$, where n_i is the number of moles of i adsorbed to surface area S (in m^2 or cm^2). If the surface area of the adsorbent is not known, the amount of adsorbed substance per g of adsorbent is used. In the ideal case, the adsorbent has an energetically homogeneous surface which is saturated with a monomolecular layer of adsorpt. The ratio $\Theta = \Gamma_i/\Gamma_\infty$ is the degree of coverage, where Γ_∞ is the saturation concentration.

In physical A., a temperature- and pressure-sensitive equilibrium is established between the concentration c_i of the adsorpt in the homogeneous phase and on the surface concentration Γ_i. The dependence of Γ_i on the concentration c_i or partial pressure p_i of gaseous substances at constant temperature is called the ***adsorption isotherm***: $\Gamma_{i,T} = f(c_i \text{ or } p_i)$. The dependence of Γ_i on temperature at constant pressure p_i is

the ***adsorption isobar*** $\Gamma_{i,p}D = f(T)$. The ***adsorption isoster*** shows the concentrations c_i which lead to the same surface concentration Γ_i at different temperatures: $c_i,\Gamma = f(T)$.

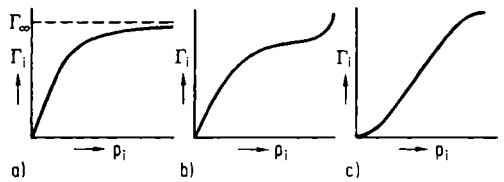
In practice, the most important of these curves are the A. isotherms. At very low coverage, the amount of adsorbed substance increases almost linearly with the concentration. At very high concentrations, it approaches a limiting value Γ_∞, which can be regarded as monomolecular coverage of the surface. However, for many adsorbents, there is then a renewed increase which can be caused by formation of several layers of the adsorbed substance, or by capillary condensation of the this substance in micropores of the adsorbent.

There are various mathematical approximations to describe the A. isotherms of gases on solids:

1) *Freundlich's A. isotherm*: $\Gamma_i = \alpha p_i^\beta$, where p_i is the partial pressure of the adsorpt, α and β are constants; 2) *Langmuir's A. isotherm*: $\Gamma_i = \Gamma_\infty \alpha p_i/(1 + \alpha p_i)$; 3) *Brunauer, Emmett and Teller's A. isotherm* (BET equation): $\Gamma_i = \Gamma_\infty \alpha p_i/(p_{i0} - p_i)[1 + (\alpha - 1)p_i/p_{i0}]$, where Γ_∞ is the maximum surface concentration in a monolayer and p_{i0} is the saturation vapor pressure of the pure liquid adsorpt. This equation applies to multi-layer adsorption. 4) the *Gibbs A. isotherm* gives the amount of a substance adsorbed to the surface of a liquid:

$$\Gamma_i = -\frac{c_i}{RT}\left(\frac{\partial \sigma}{\partial c_i}\right)_{p,T,O}$$

Here c_i is the concentration of substance i in the interior of the liquid phase, R is the general gas constant, T is the temperature in K, and $(\delta\sigma/\delta c_i)$ is the change in surface tension σ of the liquid when the concentration of surface-active substance i changes.



Various types of adsorption isotherms.

When gaseous compounds are adsorbed at high pressures by porous adsorbants, the gases condense in the pores (*capillary condensation*).

For practical applications, the most important A. processes are those on highly disperse solids, which are often porous as well; these have large specific surface areas. Examples are activated charcoal, molecular sieves and aluminum oxide. They are used for selective removal of certain impurities from gaseous and liquid mixtures (e.g. to decolor solutions, remove sulfur from smoke and to filter air in gas masks), to remove residual gases in high-vacuum systems (getter pumps) and for separations (see Parex process), etc. In heterogeneous Catalysis (see), the A. of reactants on the catalyst surface is essential. A. is also an integral part of the process of gas and adsorption chromatography. Some industrially important applications of A. are listed in the table.

Important industrial adsorption process

Adsorbed compound	Adsorbent
a) from the gas phase	
Water	8-Al_2O_3, molecular sieves, silica gel
Hydrocarbons	Activated charcoal
Solvents, e.g. halomethanes	Activated charcoal, silica gel
Sulfur compounds	Fe_2O_3, ZnO
Paraffins (parex process)	Molecular sieve
b) from the liquid phase	
Softening and deionizing of water	Ion exchangers
Removal of phenols from sewage	Activated charcoal,
Paraffins (molex process)	Molecular sieve
p-Xylene (parex/UOP process)	Molecular sieve
Olefins (olex process)	Molecular sieve

Adsorption chromatography: a separation method based on the difference in adsorption of molecules to a condensed phase (see Adsorbent) whose activity depends on the nature of the material and its surface characteristics (particle size, porosity). In A., the compounds are repeatedly adsorbed and desorbed, resulting in establishment of an equilibrium. The differences in the structures of the various adsorbates are reflected by differences in the strength of their interactions with the adsorbent, and these lead to differences in their migration rates and thus to separation. Solid adsorbants such as aluminum oxide, silica gel, activated charcoal, zeolites or starch, polyamide or dextran gels are generally used. The mobile phase can be selected from an eluotropic series of solvents (see High performance liquid chromatography). A. can be done as gas-solid or liquid-solid chromatography in columns or layers (see Thin-layer chromatography). Additional separation effects are obtained because of specific interactions (ion-exchange, biospecific affinity, molecular sieve effect, formation of inclusion compounds). Affinity chromatography (see) is a special form of A.

Adsorption isobar: see Adsorption.

Adsorption isoster: see Adsorption.

Adsorption isotherm: see Adsorption.

Adsorption charcoal: same as activated charcoal; see Charcoal.

Adsorptive: the substance enriched by adsorption, in the isolated state.

Adumbran: see Oxazepam.

A_E reaction: see Electrophilic reactions.

Aerogel: see Permeation chromatography.

Aeration element, *Evans element*: a concentration element formed by differential aeration of the electrolyte. Metal goes into solution at the poorly aerated local anode, and the electrolyte becomes acidic through hydrolysis. At the well aerated local cathode, oxygen is reduced to the hydroxide ion, which causes the pH value to rise. The oxygen corrosion of iron in aqueous solution usually occurs via many parallel A. The local corrosion in cracks and holes (see Crack corrosion; Pitting corrosion) can be considered aeration corrosion.

Aerosol: a dispersion of solid or liquid particles in a gas. Fine dusts, mists and smoke are examples of A. Clouds of fine ice particles (cirrus clouds) or water

droplets occur naturally in the atmosphere; in addition natural A. occur as results of volcanic eruptions and forest fires. Anthropogenic A. are the undesirable byproducts of industrialization: exhaust, smoke, dust and smog. Natural A. act as nucleation centers for the condensation of water vapor; they also serve as catalysts of atmospheric chemical reactions between pollutant gases, such as chlorine, nitrogen oxides and sulfur oxides. Anthropogenic A. cause considerable damage to the environment, although they may also be applied deliberately as fertilizers and pesticides in agriculture. Nearly all chemical weapons would be used in the form of A.

A. particles acquire electric charge by absorption of ions (or electrons) from the atmosphere; these charges are usually small and vary from one particle to the next. If the particles are produced by dispersion, positive, negative and neutral particles are all generated by the process. The number of charge carriers per particle depends greatly on its nature; A. of nonpolar liquids are usually weakly charged, while water droplets are highly charged (waterfall electricity, for example). A. can be destroyed by application of a centrifugal force, an electrical field or filtration.

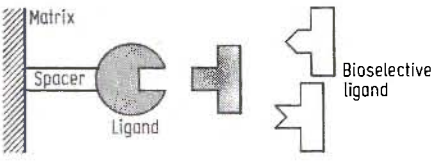
AES: 1) abb. for atomic emission spectroscopy. 2) abb. for Auger electron spectroscopy.

Aesculetin: see Coumarin, Table.

Affination: see Parting.

Affinity: an historical term, now obsolete, for the tendency of substances to react with each other. The heat of reaction was formerly considered a measure of the A. (see Berthelot-Thomsen principle). In Thermodynamics (see), the maximum useful work $\Delta_R G$ is equal to the A.: $A = -\Delta_R G$.

Affinity chromatography: a special form of Adsorption chromatography (see) in which the adsorbent is biospecific. For example, specific interactions between antibodies and antigens, enzymes and their inhibitors, nucleic acids of complementary sequences, lectins and polysaccharides, avidin and biotin or receptors and hormones can be utilized. The stationary phase consists of the bioselective *ligand* chemically bound (by esterification, azo-coupling, etc.) to an inert, porous *matrix* (agarose gel, glass beads, cellulose, polyacrylamide, cross-linked dextrans). Since the active center of a biological substance is often deep inside the molecule, the capacity of the adsorbent can often be increased by introducing *spacers* between the matrix and ligand. This reduces steric hindrance to binding of the two biological partners. Like the matrix, the ligand should be inert (fig.). In A., the components with selective affinity to the ligand are retained, while other substances are immediately eluted. The bound substance can then be eluted in pure form using a solvent which has been altered in some way (ionic strength, pH, addition of free ligand).

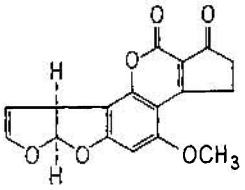


Affinity chromatography

A. is an important method in biochemistry. It is used routinely to isolate specific sequences of DNA, antibodies, enzymes, etc.; it can also be used to fractionate cell cultures.

Affinoelectrophoresis: see Electrophoresis.

Aflatoxins: metabolic products of *Aspergillus flavus* and other molds. The A. are derivatives of furocumarin, and are biosynthesized as Polyketides (see). The main product is $A.B_1$ (Fig.). The A. are colorless and lipophilic, and are highly carcinogenic (liver). A. diffuse into the food beyond the area occupied by the mold. Their effect is due to covalent binding to the DNA of the cell. The A. were discovered in 1960.



Aflatoxin B_1

AFS: abb. for Atomic fluorescence spectroscopy (see).

Ag: symbol for Silver (see).

Agar: a substance obtained from various red algae, especially those of the genuses *Gelidium* and *Gracilaria*. A. is more than 90% polysaccharides, and contains 0.3 to 0.7% sulfur in the form of sulfate monoesters. The component with the greatest tendency to swell is *agarose*, which makes up about 70% of A. Agarose is a linear polysaccharide consisting of alternating units of 3-O-substituted β-D-galactopyranose and 4-O-substituted 3,6-anhydro-α-L-galactopyranose. To obtain A., the algae are dried, bleached and extracted with boiling water. The extract is purified and solidified by cooling. A large part of the water-soluble impurities can be removed from the partially dehydrated gel by freezing it. Agarose can be separated from agaropectin, which also contains uronic acids and pyruvic acid, by utilizing the differences in solubilities of the acetates.

A. swells in water and when heated, forms a clear solution. When it is cooled, as little as 0.5 to 1.0% in solution gives a stable gel. A. is used in the food industry as a gelling agent and in pharmaceutical preparations. Because of its ability to swell, it is used as a mild laxative. Agar gels are used as carriers for electrophoresis and in microbiology, as nutrient media for microorganisms. Special agarose preparations, such as Sepharose, are used in gel chromatography.

Agarose: see Agar.

Agarose gel: see Permeation chromatography.

Agent Orange: a term for a herbicide consisting of equal parts of the butyl esters of 2,4-dichloro- and 2,4,5-trichlorophenoxyacetic acid. It was used by the US Army in the Vietnam War to defoliate forests. The severe consequences of use of this herbicide are due to the presence of approximately 40 g/t of the byproduct 2,3,7,8-Tetrachlorodibenzo-1,4-dioxin (see).

Aggregate state: a physical state of matter. The three classical A. are the solid, liquid and gas states;

plasma is often called the fourth A. The atoms, ions or molecules of a substance attract each other to a greater or lesser degree, and in the absence of thermal motion, these attractive forces would bind them rigidly together. The state of a given substance at any temperature is determined by the strength of the attractive forces relative to the tendency of thermal motions to disperse the particles into a gas.

Solids have the highest degree of order. In the limiting case of the *ideal solid*, only the forces of interaction affect the particles and they have no kinetic energy. They are arranged with complete regularity in a three-dimensional lattice; there is a strict *long-range order* (see Crystal). This state is most closely approximated at low temperatures and high pressures, but even under these conditions, it is never completely realized. Even at absolute zero, particles have a certain amount of kinetic energy, called the zero-point energy, which causes them to vibrate about their equilibrium positions. As the temperature increases, the vibrations become much more vigorous. In *real solids*, there are in addition imperfections in the regular arrangement of the particles. The model of the *perfect solid*, which has no such structural or chemical Crystal lattice defects (see), but in which the particles do vibrate thermally, has been closely approximated in a few cases by Crystal growing (see). Solids which do not have long-range structural order are called *Amorphous* (see); they are relatively rare, compared to crystalline solids. Because their constituent particles have fixed positions and because the interactions between them are strong, solids have fixed shapes and volumes.

A ***gas*** is the A. with the lowest degree of order. The average distance between gas particles is very large compared to their own size, and they move constantly in random directions which are frequently changed by collisions with other particles or the walls of the vessel (see Kinetic gas theory). In the limiting case of the *ideal gas*, which is approximated by real gases at high temperatures and low pressures, the particles do not exert any forces on each other, and their motion is completely random. In addition, the volume of the particles is so small compared to the total volume available to them that it can be ignored. All *real gases* deviate from this ideal state to a greater or lesser degree. A gas will fill the entire volume available to it, so it has no fixed shape. Gases are fully miscible with one another in any proportions.

Liquids have a position intermediate between solids and gases. They display a definite *short-range order*; there is a certain regularity of orientation and distance between immediate neighbors at any time, and this regularity approaches that of a crystal lattice. However, due to the constant thermal motion of the particles, this order is much weaker even for next-nearest neighbors, and at a distance of a few particle diameters, it cannot be recognized at all. The short-range order is dynamic; it is limited not only in spatial dimensions, but in time as well. Because of the irregular motions of the particles, the ordered microregions are constantly formed and dispersed, and each particle's position changes both in space and with respect to its neighbors. There is still no complete structural theory of liquids capable of accounting for all their macroscopic properties. Because of the ease with which their particles shift positions, liquids have no fixed shapes; they adopt the shape of the vessel and develop flat surfaces due to the effect of gravity. However, because the particles are relatively densely packed, they resist changes in volume.

The degree of order in the three A. can be visualized with the help of *radial density distribution functions W(R)* derived from diffraction experiments (Fig. 1). In a coordinate system with its origin on an arbitrarily chosen particle, *W(R)* is the probability that a vector of length *R* starting at the origin will end on another particle. The periodic spacing of the maxima of *W(R)* for a solid indicates the long-range order of the crystal. In liquids, the first maximum has the same position and height as the first maximum in the corresponding solid, but subsequent maxima decline rapidly, indicating the spatial limitation of the short-range order. For a gas, beyond a certain distance determined by the diameter of the particle, the probability of finding another particle at any given distance is equal to that at any other distance.

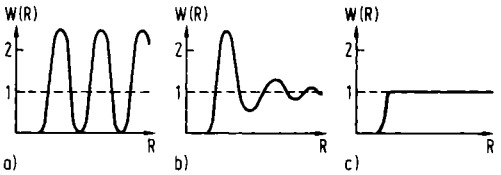


Fig. 1. Radial distribution function *W(R)* of a solid *(a)*, a liquid *(b)* or a gas *(c)*.

All elements and many compounds can exist in all three A. The transitions between them occur at characteristic temperatures, which depend on the pressure; decreases in order are accompanied by absorption of heat, and increases in order, by release of heat. These phase changes are described by the Clausius-Clapeyron equation. The three A. of a substance can be plotted in a diagram of state, e.g. a *p-T* diagram. The state surfaces of each A. are separated by curves, at which the phase changes occur. The phase-change curve between the liquid and gas states ends at a critical point, above which it is no longer possible to distinguish between liquid and gas. Each A. can occur in a very broad temperature range. The range of existence and the relationships for the transitions between A. can be seen in Fig. 2. The diagram includes the ***plasma*** into which a gas is converted at

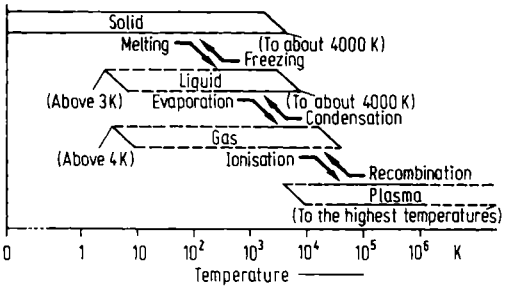


Fig. 2. Ranges of existence of the individual aggregate states.

sufficiently high temperatures. Since the plasma state is fundamentally different from the other A., it can be considered a fourth A.

The boundary between the A. is not always clear. Liquid crystals (see) and Amorphous solids (see) are intermediate states between solids and liquids.

The thermodynamic Phase (see) must not be confused with the concept of A. For example, two immiscible liquids form two phases, but are in a single A.

Aggregate system: a macroscopic system of aggregated particles. Its properties are determined by the nature and strength (range) of the interaction between the particles. A highly ordered A. with a periodic arrangement of particles extending over a long range is a crystal. Lower-order A., in which the order extends only to the immediate neighborhood of a given particle (short-range order) include amorphous solids and liquids. Liquid crystals occupy an intermediate position.

Aggregation number: see Micelle.

Aglycon: the non-sugar component of a Glycoside (see).

Agrochemicals: compounds used in agriculture and associated technologies. A. include fertilizers, plant and animal foods (including micronutrients), pesticides, growth regulators, soil modifiers, preservatives for stored grains and produce, etc.

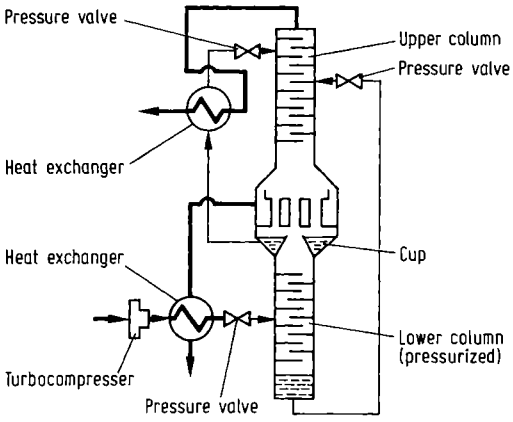
Agroclavine: see Ergot alkaloids.

AH salt: see hexamethylenediamine.

Air analysis: chemical and physical methods for quantitative determination of the concentration of air pollutants, both indoors and outdoors. For indoor monitoring, semiquantitative analyses using standardized test kits are usually sufficient, but monitoring of outdoor pollutants requires highly sensitive and selective methods. Gaseous pollutants are usually sampled by impingers, and measured by colorimetric tests, titration, ion-sensitive electrodes, atomic absorption spectrophotometry or other methods. There are automatic, continuously recording devices which measure conductivity. To measure the amount of particulates, a certain volume of air is sucked through a special filter. Sedimentation particulates are collected for 30 days in vessels with known trapping surface and determined gravimetrically.

Air fractionation: low-temperature separation of air into its component gases, chiefly nitrogen and oxygen, but also the noble gases argon, krypton, xenon, neon and helium. As a rule, A. involves the following steps: compression, purification (removal of water, carbon dioxide and traces of hydrocarbons), cooling (in heat exchangers where the separated gases are warmed as they cool the incoming air), refrigeration to compensate for heat flow into the system (heat leaks in the entire system, losses in heat transfer, withdrawal of liquefied gases), and low-temperature distillation in a plate column.

The liquefaction of air, and later its fractionation, were first achieved by Linde. The classical high-pressure Linde process is shown schematically in the figure.



Air fractionation by the Linde process.

Air liquefaction: see Gas liquefaction, see Air fractionation.

Air pollution: in the widest sense, a term for solids, liquids and gases which were not originally present in the atmosphere. In a narrower sense, only those substances which have entered the air through human activity (***anthropogenic pollutants***) are included. Natural A. is caused, for example, by volcanoes, decomposition of organic materials, wildfires and natural dust. The main sources of anthropogenic A. are industry, transportation, space heating and agriculture. Of the industrial sources, heating and electric power plants are the major contributors; they are followed by the chemical industry, metallurgy, the cement industry and the ceramic industry. Combustion of fossil fuels (other than natural gas) converts the sulfur in the fuel to sulfur dioxide, and most of this escapes with the smoke.

A mixture of smoke and fog is called "smog", and the term has become widely synonymous with A. There are two major types of smog: industrial and photochemical. Industrial (London-type) smog consists mainly of sulfur trioxide (SO_3) and particulates (ash, soot and partially burned hydrocarbons) formed by combustion of fossil fuels. Sulfur trioxide is the anhydride of sulfuric acid; atmospheric moisture converts it to the acid and precipitation washes it out of the air as *acid rain*. In aerosol form, H_2SO_4 is damaging to human and animal lungs, metals and building materials such as marble. In the form of acid rain, H_2SO_4 has caused heavy losses of fish in lakes throughout northeastern North America and Europe.

Photochemical (Los Angeles type) smog is produced by the action of ultraviolet light on the products of internal combustion engines: nitrogen oxides and unburned hydrocarbons. It contains little or no sulfur trioxide. The major components of photochemical smog are ozone, peroxyacyl nitrogen, peroxides, and various hydrocarbons. This type of smog damages plant life and is thought by some to be responsible for the dying of forests in Europe in the past 25 years. Other significant pollutants, which do not necessarily create smog, are fluorine compounds, nitrogen oxides, hydrogen chloride and chlorides, ammonia, chlorofluorocarbons and heavy metal com-

pounds. Hydrogen fluoride, hydrogen chloride and nitric acid contribute to acid rain (see above). The presence of heavy metals in the soil is damaging to both plants and the animals which feed on them. The presence of chlorine compounds in the atmosphere catalyses the destruction of stratospheric ozone, which protects the surface of the earth from solar ultraviolet radiation; the decrease has recently become statistically significant.

Because A. is noxious and even small amounts interfere with a sense of well being, the concentration of pollutants in air must be limited. Governments establish limits for the maximum acceptable concentrations of various pollutants in the workplace and in the atmosphere outside the workplace (see Indoor air quality). In both cases, both chronic and peak values are regulated to prevent damage by extremes.

A. can be prevented both by engineering in new plants and vehicles and by removal of pollutants by Waste gas purification (see) or by Flue gas desulfurization (see). The construction of very high smokestacks prevents concentrated A. near the plant producing the smoke, but is believed to be responsible for acid precipitation falling hundreds of kilometers away in nonindustrial areas. In the Vehicle exhaust (see) sector, both reduction of emissions and better organization of traffic can make significant contributions. A. is monitored by methods of Air analysis (see).

Ajmaline: see Rauwolfia alkaloids.

Al: symbol for Aluminum.

Ala: abb. for Alanine (see).

Alachlor: see Acylaniline herbicides.

Alamethicin: a membrane-active peptide antibiotic isolated from culture filtrates of the fungus *Trichoderma viride*: Ac-Aib-Pro-Aib-Ala-Aib-Ala-Gln-Aib-Val-Aib-Gly-Leu-Aib-Pro-Val-Aib-Aib-Glu-Gln-Phol. A. is an amphiphilic polypeptide which, like ***suzukacillin*** and ***trichotoxin***, can generate a fluctuating, voltage-dependent ion flux with action potentials. It is therefore of great interest as a model system for nerve conduction. Aggregation of these peptides forms pores with different conductive capacities, so that mechanisms of membrane penetration can be studied. A. was originally thought to have a cyclic octadecapeptide structure, but in the revised linear structure, the *N*-terminal α-aminoisobutyric acid residue (Aib) is acetylated, and the *C*-terminus is bound to a phenylalaniol group (Phol). Suzukacillin A and trichotoxin A40 are natural analogs of A. with similar membrane-penetrating properties; they have a high degree of homology with A.

Alanates: hydrido complexes of aluminum with the composition $M[AlH_4]_n$. The tetrahedral AlH_4^- anion is formally the product of addition of a hydride ion to aluminum hydride, $(AlH_3)_x$. The most important is Lithium alanate (see), which is widely used as a reducing agent. Other elements in Groups Ia to IIIa also form A.

Alane: same as aluminum hydride.

Alanine, ***aminopropionic acid***, abb. ***Ala***: 1) α-Alanine, CH_3-$CH(NH_2)$-COOH is a proteogenic Amino acid (see). It is one of the main components of silk fibroin. The chemical synthesis according to Strecker and Bucherer gives an 88% yield of DL-A. which, in the form of *N*-acetyl- or *N*-chloroacetyl-DL-A., is converted to L-A. by hydrolysis catalysed by immobilized acylase. A biotechnological pathway to L-A. starts from L-aspartic acid, which is converted to L-A. by microbial or enzymatic decarboxylation. In the organism, A. is formed by transamination of pyruvic acid. *N*-Methylalanine is used to dissolve hydrogen sulfide from industrial gases (sulfosolvane process).

2) β-Alanine, H_2N-CH_2CH_2-COOH, is an important, naturally occurring β-amino acid. It is formed by enzymatic decarboxylation of aspartic acid, and is a component of anserine, carnosine and coenzyme A.

Albumins: simple proteins consisting largely of glutamic and aspartic acids (20 to 25%), leucine and isoleucine (up to 16%) and relatively large amounts of cysteine and methionine, but little glycine (< 1%). The A. are very soluble in water and crystallize well; they can be precipitated by high concentrations of netural salts. Their isoelectric points are in the weakly acid range. The most important animal and plant A. are listed below. ***Ovalbumin*** from chicken eggs has M_r 44,000. It has a phosphate group esterified to serine and a carbohydrate component. The heat-resistant ***lactalbumin*** is present in all types of milk; it contains 123 amino acid residues (M_r 14,176) and four disulfide bridges. ***Serum albumin*** makes up to 60% of the dry mass of blood serum; its M_r is 67,500. It has a high binding capacity for calcium, sodium and potassium ions, fatty acids and drugs. The main function of the serum A. is maintenance of the osmotic pressure in the blood. Some important plant A. are the toxic ***ricin*** from *Ricinus* seeds (castor oil is produced from *Ricinus communis*), ***leucosin*** from wheat and other grains, and ***legumetin*** from legumes.

Alcohol: see Alcohols; in general usage, the same as ethanol.

Alcoholates, ***alkoxides***: ionic derivatives of alcohols formed by substitution of a metal of the first to third main group for the H of the OH group. The most common A. contain Na, K, Mg or Al. Sodium methylate, CH_3ONa, potassium *tert.*-butylate, $(CH_3)_3COK$, magnesium methylate, $(CH_3O)_2Mg$ and aluminum isopropylate $[(CH_3)_2CHO]_3Al$ are of practical importance. A. are moisture-sensitive solids which hydrolyse immediately on contact with water, forming the alcohol and metal hydroxide: $CH_3O^-Na^+ + H_2O \rightarrow CH_3OH + NaOH$. The aluminum A. are relatively stable, and can be distilled in vacuum without decomposition. A. are readily soluble in excess alcohol. They are used as nucleophiles for syntheses in anhydrous solutions.

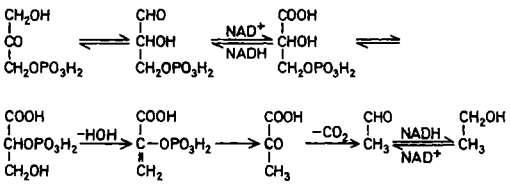
A. are produced by reaction of the metals with anhydrous alcohols: CH_3-CH_2-OH + Na → CH_3-CH_2-O^-Na^+. Sodium and potassium react spontaneously and release so much heat that the reaction mixture may have to be cooled. Magnesium and aluminum have to be activated by treatment with iodine or mercury(II) chloride. The reaction releases atomic hydrogen, which can be used for hydrogenation. A. react with haloalkanes (see Williamson synthesis) to form ethers, which is especially useful as a method for producing unsymmetric ethers: R^1-Cl + $NaOR^2 \rightarrow R^1$-O-R^2 + NaCl.

A. are used as condensation reagents for the Claison condensation (see) and as catalysts for organic redox reactions (see Oppenauer oxidation,

Meerwein-Ponndorf-Verley reduction). The reaction of reactive metals with alcohols is important in the synthesis of anhydrous alcohols, e.g. with magnesium methylate, and for safe disposal of excess sodium or potassium.

Alcohol dehydrogenases: enzymes which catalyse the reversible oxidation of primary and secondary alcohols to the corresponding aldehydes or ketones; NAD^+ is the hydrogen acceptor. The most famous example is ***yeast A.***, a zinc-containing protein of M_r 145,000. It consists of four subunits, each with a binding site for NAD^+/NADH; as the last enzyme in alcoholic fermentation, it catalyses the conversion of acetaldehyde to ethanol. A. are found in all organisms. To determine the concentration of ethanol in the blood, the change in optical extinction of a solution of NAD^+/NADH at 340 nm in the presence of the enzyme is measured.

Alcoholic fermentation: anaerobic conversion of glucose to ethanol and carbon dioxide, especially by yeast or enzymes from yeast. The process is used on an industrial scale to produce ethanol. The overall equation for A. is $C_6H_{12}O_6 + 2\ H_3PO_4 + 2\ ADP \rightarrow 2\ C_2H_5OH + 2\ CO_2 + 2\ H_2O + 2\ ATP$; the conversion of ADP to ATP supplies the cell with the energy needed to maintain its metabolism. The glucose is converted to pyruvic acid by the reactions of Glycolysis (see). Pyruvate decarboxylase converts pyruvic acid to acetaldehyde, which is then converted to ethanol by alcohol dehydrogenase; NAD^+ is simultaneously regenerated:



A. depends on the presence of a sufficient concentration of phosphate, a temperature between 30 and 37 °C, a pH between 4.5 and 5.7, and a sugar concentration of 20 to 25%. Higher sugar concentrations and alcohol concentrations above 20% inhibit growth of the yeast cells.

The fermented liquids generally contain 10 to 18% ethanol; the maximum yield is 0.5 kg ethanol per kg glucose.

A byproduct of A. is glycerol, which may account for up to 3% of the sugar consumed. This yield can be considerably increased by addition of sodium hydrogensulfite to the fermentation liquid. This is "Neuberg's second type of fermentation". The acetaldehyde which normally acts as hydrogen acceptor is trapped by the hydrogensulfite, and the reducing equivalents of $NADH + H^+$ are transferred to dihydroxyacetone phosphate. The resulting glycerol phosphate is then dephosphorylated to glycerol. "Neuberg's third type of fermentation" occurs when an alkali added to the fermentation causes a Canizzaro reaction to take place, converting acetaldehyde to ethanol and acetic acid; dihydroxyacetone phosphate acts as the hydrogen acceptor and leads to production of glycerol. $2\ C_6H_{12}O_6 + H_2O \rightarrow CH_3\text{-}CH_2\text{-}OH + CH_3\text{-}COOH + 2\ CO_2 + 2\ CH_2OH\text{-}CHOH\text{-}CH_2\text{-}OH$.

Historical. A. was known several thousand years ago, and is considered the oldest biotechnology. The first scentific studies were made by Lavoisier (1789), who realized that carbohydrates are converted to alcohol and carbon dioxide. In 1815, Gay-Lussac established the net equation for A. Around 1857, Pasteur promoted the hypothesis that A. could only occur in the presence of living organisms ("vitalistic" fermentation theory). In 1897, Buchner showed that A. could be carried out by cell-free preparations from yeast. This discovery was the starting point for modern enzymology. Further important studies on the complicated course of fermentation reactions were done by Neuberg (1877-1956), Harden (1865-1940), Embden (1874-1933) and Meyerhof (1884-1951).

Alcoholometry: determination of the alcohol content of aqueous ethanol solutions using an alcoholometer (density gauge). The instrument is calibrated so that the ethanol content can be read directly in mass % or volume % (Table).

Density of solution	Mass %	Vol. %	g alcohol per liter
0.998	0.15	0.19	1.5
0.990	4.70	5.90	46.5
0.980	11.47	14.24	112.4
0.970	19.11	23.48	185.4
0.960	26.15	31.80	251.0
0.950	32.24	38.80	306.3
0.940	37.62	44.80	353.6
0.930	42.57	50.15	395.9
0.920	47.26	55.07	434.8
0.910	51.78	59.69	471.2
0.900	56.18	64.04	505.6
0.890	60.50	68.21	538.5
0.880	64.78	72.22	570.1
0.870	69.01	76.06	600.4
0.860	73.20	79.74	629.5
0.850	77.32	83.26	657.2
0.840	81.38	86.60	683.6
0.830	85.37	89.76	708.6
0.820	89.24	92.69	731.8
0.810	92.25	95.38	752.9
0.800	96.48	97.77	771.8

Alcohols: organic compounds containing hydroxyl (-OH) groups on sp^3-hybridized C atoms. Formally, the A. can be derived by substitution of H atoms in hydrocarbons: Alkanols (see) from alkanes, Cycloalkanols (see) from cycloalkanes, etc. The C atom to which the OH group is bound can also be part of a side chain of an aromatic compound, as in Benzyl alcohol (see), or of a heteroaromatic compound, as in Furfuryl alcohol (see).

Mono-, di-, tri- and poly A. contain the corresponding number of OH groups, each bound to a different C atom. Some important monoalcohols are Methanol (see) and Ethanol (see); Glycol (see) and Glycerol (see) are simple di- and trialcohols, respectively (Tables 1 and 2). Reduction of monosaccharides leads to hexaalcohols, such as D-Glucitol (see) and D-Mannitol (see). A primary A. is one in which the OH group is bound to a terminal C atom; a secondary A. is one in which the C to which the OH is bound has bonds to two other carbons, and a tertiary A. is one in which the C to which the OH is bound is

linked to three other C atoms. Thus the general formulas are:

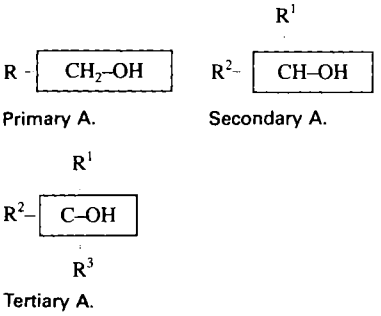


Table 1. Homologous series of monoalcohols

Methanol	CH_3-OH
Ethanol	CH_3-CH_2-OH
Propan-1-ol	$CH_3-CH_2-CH_2-OH$
Propan-2-ol	$CH_3-CH(OH)-CH_3$
Butan-1-ol	$CH_3-CH_2-CH_2-CH_2-OH$
Butan-2-ol	$CH_3-CH_2-CH(OH)-CH_3$
2-Methyl-propan-1-ol (Isobutanol)	$CH_3-CH(CH_3)-CH_2-OH$
2-Methyl-propan-2-ol (tert-Butanol)	$CH_3-C(CH_3)_2-OH$

Table 2. Some di- and polyalcohols

Glycol (Ethan-1,2-diol)	$HO-CH_2-CH_2-OH$
Propylene glycol (Propan-1,2-diol)	$HO-CH_2-CH(OH)-CH_3$
Propan-1,3-diol	$HO-CH_2-CH_2-CH_2-OH$
Glycerol (Propan-1,2,3-triol)	$HO-CH_2-CH(OH)-CH_2-OH$
Pentaerythrol	$HO-CH_2-C(CH_2-OH)_2-CH_2-OH$

The simplest primary A., methanol, is obtained by formal substitution of R by H.

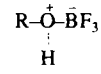
The monoalcohols are named by combination of the root name for the hydrocarbon skeleton with the suffix -ol. If the root ends in -e, this is elided. Isomers are distinguished by indicating the position of the OH group by a numeral in front of the suffix, e.g. propan-2-ol. In radicofunctional nomenclature, the word "alcohol" is added to the name of the radical, as in methyl alcohol. Thus the simplest tertiary A. can be named in three ways: *tert.*-butanol, *tert.*-butyl alcohol and 2-methylpropan-2-ol. When two or more OH groups are present, the suffixes -diol, -triol, etc. are used, and the positions of the OH groups are indicated, using the smallest numbers possible, e.g. butan-1,4-diol. Some trivial names are still accepted in the IUPAC system.

Properties. Low-molecular-weight A. are liquids with a typical kind of odor and a burning taste; compared to hydrocarbons of similar size, they have relatively high boiling points, due to intermolecular hydrogen bonding. This property is even more pronounced in the viscous polyalcohols, such as glycols or glycerol. A. with higher molecular weight are solids with weak odors. Because of the interactions of the hydrophilic polar OH group with water molecules, the lowest A. are miscible with water in all proportions. The boundary of solubility is found at C_4 for monoalcohols, but is much higher for polyalcohols. *tert.*-Butanol is still miscible with water in any proportion, while the isomeric amyl A. are practically insoluble in water; here the hydrophobic character of the alkyl radicals predominates. D-Glucitol and mannitol are readily soluble in water, but they have lipophilic properties; they are not soluble in diethyl ether or ethanol. Many A. have physiological effects (see Methanol, Ethanol, Fusel oil). The lower monoalcohols are combustible and ignite readily. Methanol, which can be synthesized on a large industrial scale, and ethanol, which is also produced on a large scale, by fermentation, can be used as fuels for motor vehicles. A. give neutral reactions with acid-base indicators, but they can form salts with reactive metals of the first to third main groups of the periodic system. Substitution of a metal atom for the H atom of the OH group produces an Alcoholate (see): $CH_3OH + Na \rightarrow CH_3O^-Na^+ + H$. The reaction is also of practical interest for producing nascent hydrogen, which can react immediately, in the alohol solution, with a substrate (see, for example, Bouveault-Blanc reduction). The reaction can also be used to produce absolutely dry A. with magnesium methylate, or for the safe disposal of alkali metals. The latter two applications are based on the ease of hydrolysing the alcoholates.

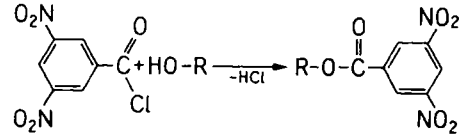
In terms of the Brönsted acid-base theory, A. are ampholytes:

$$ROH \rightleftharpoons RO^- + H^+; \quad ROH + H^+ \rightleftharpoons R\text{–}\overset{+}{O}H$$

However, A. are weaker acids than water, with pK values around 16, so that there is practically no spontaneous dissociation. The formation of alkoxonium ions, which can appear as intermediates in chemical reactions, occurs only with strong Brönsted acids or with Lewis acids, such as BF_3: R-O-H + $BF_3 \rightarrow$



Reactions. A. combine with inorganic acids to form alkyl halides, alkyl nitrites, alkyl nitrates, alkyl sulfates, dialkyl sulfates and trialkyl phosphates, and with carboxylic acids or their anhydrides to form esters: $R\text{-}CH_2\text{-}OH + HBr \rightarrow R\text{-}CH_2\text{-}Br + H_2O$; $C_2H_5OH + R\text{-}COOH \rightleftharpoons R\text{-}COOC_2H_5 + H_2O$. The reaction of A. with 3,5-dinitrobenzoyl chloride to form 3,5-dinitrobenzoates is used to identify them:



The hydrochloric acid released is neutralized by a base.

When heated with sulfuric, phosphoric or oxalic acid, A. undergo intramolecular dehydration to form alkenes or an intermolecular water loss to form ethers. The two reactions compete with one another. High temperatures promote alkene formation, while lower temperatures promote ether formation: $C_2H_5OH \rightarrow CH_2{=}CH_2 + H_2O$, $2\ C_2H_5OH \rightarrow C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$.

The situation is similar in gas-phase hydrogenation on Al_2O_3. At 350 to 400 °C, alkenes are formed almost without byproducts, while at 260 °C, the products are mainly ethers. The ease of intramolecular water elimination (alkene formation) increases in the order primary A. < secondary A. < tertiary A. Ether formation is promoted by an excess of A.; primary A., as would be expected, are more likely to form symmetric ethers than are tertiary A.

In the formation of alkenes, the thermodynamically more stable product is formed (Zajcev orientation); for example, but-2-ene is formed from butan-2-ol, not but-1-ene:

$$CH_3CH_2\text{–}CH(OH)\text{–}CH_3 \xrightarrow[-H_2O]{} CH_3\text{–}CH{=}CH\text{–}CH_3.$$

A. can be oxidized or dehydrogenated to aldehydes, ketones and carboxylic acids. Primary A. produce aldehydes, which can then be further oxidized to carboxylic acids:

$$R\text{–}CH_2\text{–}OH \xrightarrow[-H_2O]{+O} R\text{–}CHO \xrightarrow{+O} R\text{–}COOH.$$

Secondary A. are oxidized to ketones:

$$R^1\text{–}CHOH\text{–}R^2 \xrightarrow[-H_2O]{+O} R^1\text{–}CO\text{–}R^2.$$

Tertiary A. are not changed in neutral or basic solution, but in acid media, they can be oxidatively degraded to their hydrocarbon skeletons. Identification of the various oxidation products is used in analytical chemistry to distinguish primary, secondary and tertiary A. Potassium dichromate in sulfuric acid, chromium(VI) oxide, *tert.*-butylchromate or a pyridine-chromic acid complex is used as oxidizing agent. Potassium permanganate or nitric acid can also be used for complete oxidation of primary A. to carboxylic acids. Activated manganese dioxide and selenium(IV) oxide are used to convert primary A. to aldehydes. Primary and secondary A. can also be oxidized to aldehydes and ketones with acetone in the presence of aluminum isopropylate (see Oppenauer oxidation). Industrially, the dehydrogenation to aldehydes or ketones is done with air oxygen on copper, silver or zinc oxide contacts at 400 to 600 °C.

Analytical. Qualitative tests are a neutral reaction and the reaction with a small amount of metallic sodium, generating hydrogen; for methanol, a test is formation of the boric acid methyl ester which burns with a green flame. The iodoform test is used for ethanol or compounds with the CH_3-CHOH- group. Primary, secondary and tertiary A. can be distinguished by their different oxidation products. These are identified in the form of esters of 4-nitrobenzoic acid or 3,5-dinitrobenzoic acid, made by reaction of the A. with the corresponding acyl chlorides. Crystalline urethanes made by reaction with aryl isocyanates may also be used. A. are identified by bands in the IR spectrum in the range from 1050 to 1300 cm^{-1} (C-O valence vibration) and between 3200 and 3700 cm^{-1} (O-H valence vibration). The position of the O-H vibration is strongly affected by the degree of association, and thus by the concentration. For example, free hydroxyl groups have absorption bands between 3590 and 3650 cm^{-1}; these bands are shifted to lower wavenumbers by intramolecular (3420 to 3590 cm^{-1}) or intermolecular (3200 to 3550 cm^{-1}) hydrogen bonds. In NMR spectra, the chemical shifts of the OH protons depend on the polarity of the O-H bond and the degree of association; in other words, these spectra are not very useful for identification of A. The mass spectra of A. often display only weak molecular peaks. The fragmentation pattern is determined by elimination of water and cleavage of the C-COH bond. The ion $[CH_2{=}OH]^+$ appears as a characteristic fragment.

Occurrence. A few A. occur in nature, in free or bound state. Glycerol, for example, is a component of lipids, and A. with higher molecular weights, such as cetyl, ceryl and myricyl A., are components of waxes. A few other biological A. of interest are geraniol and menthol, which are terpenes, farnesol, a sesquiterpene, retinol (vitamin A_1), a diterpene, and cholesterol, a steroid A.

A. can be synthesized chemically in many ways:

1) Hydration of alkenes in the presence of acids:

$$R\text{–}CH{=}CH_2 + H_2O \xrightarrow{H^+} R\text{–}CH(OH)\text{–}CH_3$$

2) Epoxidation of alkenes with subsequent hydrolysis of the epoxides (oxiranes):

$$R\text{–}CH{=}CH\text{–}R + CH_3\text{–}COOOH \longrightarrow$$

$$R\text{–}\underset{\diagdown\,O\,\diagup}{CH\text{–}CH}\text{–}R \xrightarrow{H_2O/H^+} R\text{–}CH(OH)\text{–}CH(OH)\text{–}R$$

This is done, for example, with peroxyacetic acid, or oxygen and silver oxide.

3) Addition of hypochlorous acid, HOCl, to an alkene followed by basic hydrolysis of the intermediate chlorohydrine and epoxide:

$$R\text{–}CH{=}CH_2 + HOCl \longrightarrow R\text{–}CH(OH)\text{–}CH_2\text{–}CL \xrightarrow{-HCl}$$

$$R\text{–}\underset{\diagdown\,O\,\diagup}{CH\text{–}CH_2} \xrightarrow{+H_2O} R\text{–}CH(OH)\text{–}CH_2\text{–}OH.$$

4) Reaction of ethyne with formaldehyde (see Acetylene chemistry), followed by catalytic hydrogenation of the resulting butyne-1,4-diol:

$$HC{\equiv}CH + 2\,CH_2 \longrightarrow HOCH_2{-}C{\equiv}C{-}CH_2OH$$

$$\xrightarrow{H_2/\text{Catalyst}} HO{-}CH{-}CH_2{-}CH_2{-}CH_2{-}OH$$

5) Reaction of alkyl halides with alkali hydroxides:

$$R{-}CH_2{-}Cl + OH^- \rightarrow R{-}CH_2{-}OH + Cl^-.$$

6) Hydrolysis of carboxylic acid esters which are either natural products or can be synthesized from alkyl halides.

7) Reduction of carboxylic acid esters: a) Bouveault-Blanc reduction. b) Catalytic hydrogenation using copper(II)-chromium(III) oxide mixed catalysts: $R^1\text{-}COOR^2 + 4\,H \rightarrow R^1\text{-}CH_2OH + R^2\text{-}OH$.

8) Reduction of aldehydes and ketones: a) catalytic hydrogenation with Raney nickel: $R\text{-}CHO + H_2 \rightarrow R\text{-}CH_2\text{-}OH$; b) reduction with sodium and ethanol: $R\text{-}CHO + 2\,H \rightarrow R\text{-}CH_2\text{-}OH$; c) reduction with complex metal hydrides, such as lithium aluminum hydride or sodium borohydride: $R\text{-}CHO + 2\,H \rightarrow R\text{-}CH_2\text{-}OH$; d) reduction of ketones to pinacols; e) Meerwein-Ponndorf-Verley reduction (see); f) Cannizzaro reaction (see) and Claisen reaction (see).

9) Grignard reactions with aldehydes, ketones and carboxylic acid esters: a) reactions of formaldehyde with Grignard reagents to form primary A.:

$$HCHO + RMgX \rightarrow H{-}\underset{\displaystyle H}{\overset{\displaystyle OMgX}{\underset{|}{\overset{|}{C}}}}{-}R \xrightarrow{H_2O} R{-}CH_2{-}OH.$$

b) reaction of other aldehydes, ketones and carboxylic acid esters to secondary and tertiary A. (see Grignard reaction).

10) Complete catalytic hydrogenation of phenols to cyclohexanols under pressure and at high temperatures in autoclaves.

11) Reaction of primary aliphatic amines with nitric acid: $R\text{-}CH_2\text{-}NH_2 + HNO_2 \rightarrow [R\text{-}CH_2\text{-}N{=}N\text{-}OH] \rightarrow R\text{-}CH_2\text{-}OH + N_2$.

12) Oxidation of industrially available aluminum trialkyls with subsequent hydrolysis:
$[CH_3\text{-}(CH_2\text{-}CH_2)_n]_3Al \rightarrow [CH_3\text{-}(CH_2\text{-}CH_2)_nO]_3Al \rightarrow 3\,CH_3\text{-}(CH_2\text{-}CH_2)_n\text{-}OH + Al(OH)_3$
(n = 11, 13, 15, 17).

This reaction is important for industrial production of long-chain alkan-1-ols as starting materials for detergents.

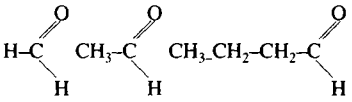
Applications. Monoalcohols of low molecular weight are used in large quantities as solvents and fuels, and in the synthesis of esters, ethers, alkenes and other organic compounds. Simple dialcohols and trialcohols are used in cosmetics, as antifreezes, and in the production of explosives, lubricants and textile conditioners.

Alcoholysis: same as Esterification (see Esters).

Aldaric acids, ***sugar dicarboxylic acids***: dicarboxylic acids with the general formula $HOOC\text{-}(CHOH)_n\text{-}COOH$. Formally, they are the products of oxidation of both terminal groups of aldoses. The names are based on the roots of the aldose names, with the suffix -aric acid. Trivial names are generally preferred, e.g. tartaric instead of threaric acid, mucic instead of galactaric acid, saccharic instead of glucaric acid. Salts and esters of glucaric acid are called ***saccharates***. Calcium saccharate is used as a concrete liquefier, and is added to calcium gluconate solutions as a stabilizer.

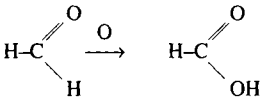
Aldazines: symmetric or unsymmetric biscondensation products of hydrazine with aldehydes. The class of Azines (see) consists of A. and ketazines.

Aldehyde: a carbonyl compound containing one or more aldehyde (-CHO) groups in the molecule. Depending on the nature of the organic residue to which the aldehyde group is bound, the A. can be classified as aliphatic, aromatic or heterocyclic. According to the IUPAC nomenclature, an aliphatic A. is named by adding the suffix "-al" to the root of the corresponding hydrocarbon skeleton name:

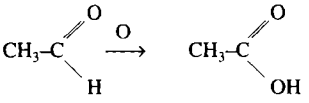


Methanal Ethanal Butanal

An older system of trivial names is also still in use; these names were derived from the Latin names of the carboxylic acids formed by oxidation of the A.:



Formaldehyde Formic acid (acidum formicium)



Acetaldehyde Acetic acid (acidum aceticum)

The aromatic and heterocyclic aldehydes, in which the aldehyde group is bound directly to a carbon atom of the ring, are usually given trivial names, e.g. benzaldehyde. Their systematic names are formed from the name of the root compound with the suffix "carbaldehyde", e.g. pyrrol-2-carbaldehyde.

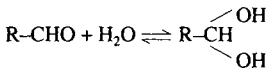
Properties. Most of the lower aliphatic A., except for the gaseous formaldehyde, are non-viscous liquids with pungent odors. As the molecular mass increases, the A. become more viscous; those with the highest molecular masses are solids. Because they do not form intermolecular hydrogen bonds, the boiling points of the A. are lower than those of the corresponding alcohols. They are generally readily soluble in organic solvents. Certain A. have pleasant, characteristic odors, e.g. benzaldehyde and cinnamaldehyde.

Except for formaldehyde, the saturated, aliphatic aldehydes are relatively non-toxic, except for their irritation of the mucous membranes. Their mildly narcotic effects are only noticeable at high

concentrations. The unsaturated aldehydes, e.g. acrolein and crotonaldehyde, are more irritating to the mucous membranes and to the external skin. The toxicity of the aldehydes generally decreases as molecular mass increases. Halogen-substituted aldehydes are considerably more irritating to the mucous membranes.

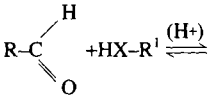
Reactions. The reactivity of the A. is due mainly to the presence of the Carbonyl group (see). In the addition and condensation reactions which are typical of the A., nucleophilic reaction partners add to the partially positive carbonyl carbon atom, while electrophilic reagents are bound to the partially negative oxygen atom (condensation). In contrast to the condensation products, most of which are stable, addition products have varying degrees of stability, depending largely on the nature of the substituents and the catalytic conditions.

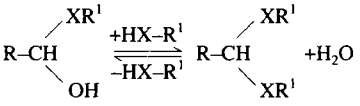
When water is added to A., the products are aldehyde hydrates (1,1-diols), most of which are unstable (see Erlenmeyer rule); the equilibrium position of the reaction



usually lies on the side of the reactants. One stable compound of this type is chloral hydrate.

Alcohols or thioalcohols can be added in analogous fashion to A. in the presence of acidic catalysts like hydrogen halides or zinc chloride. The unstable semiacetals formed thus usually react further under the reaction conditions, adding another alcohol or thioalcohol molecule, with cleavage of water, to form the acetal or thioacetal:

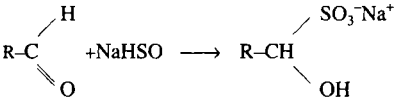




where X = O or S.

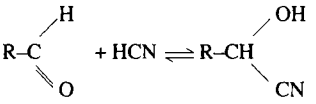
Because acetals are very stable in the presence of bases, they are often used in syntheses instead of the free A. They can be easily converted back to the A. by dilute acids. Reducing agents, such as hydrogen, lithium aluminum hydride and sodium borohydride, convert A. into primary alcohols. The reduction can be achieved by the Meerwein-Ponndorf-Verley reduction (see), which uses aluminum isopropanolate in a reversal of the reaction of the Oppenauer oxidation (see) by isopropanol. Under the conditions of the Wolff-Kishren reduction (see), A. are reductively converted to the corresponding hydrocarbons. The action of oxidation agents on A. produces the corresponding carboxylic acids. This reaction occurs very easily, since A. are reducing agents. It is therefore often used to characterize this class of compounds and to distinguish them from Ketones (see). The Tollens, Nylanders or Fehling reagent is used as an oxidation agent for this purpose.

Another well-known addition reaction of A. is the addition of sodium hydrogensulfite to form insoluble, crystalline hydrogensulfite compounds:

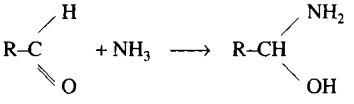


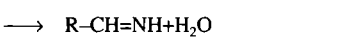
Since the bisulfide adducts can easily be removed again by dilute acids or sodium carbonate solution, this reaction is often used to purify the A.

A reaction of A. which is important for numerous syntheses is the formation of cyanohydrins by addition of hydrogen cyanide to the carbonyl group:



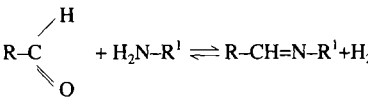
When A. react with ammonia, the first products are the aldehyde-ammonia adducts, most of which are unstable, and readily eliminate water to form aldimines:





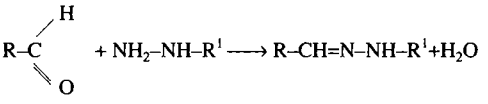
Aldimines often trimerize to triazine derivatives. In the case of formaldehyde, a further reaction produces hexamethylene tetramine. The reaction of benzaldehyde with ammonia differs from the ordinary reactions of A. with ammonia; it forms hydrobenzamide under these conditions.

A. condense with primary amines to azomethines:



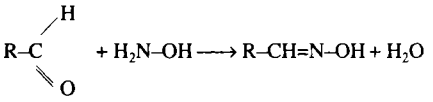
In the reaction with secondary amines, A. react with α protons to form enamines. In the absence of α-H atoms, aminals are formed. A. can be converted into secondary alcohols by Grignard reactions (see).

The condensation of A. with hydrazine or substituted hydrazines, such as phenylhydrazine, 4-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine to form the corresponding hydrazones:



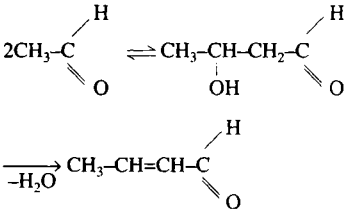
are very important, not least in the separation and characterization of A.

The condensation of A. with hydroxylamine, forming the oximes, are of similar importance:



Semicarbazones and thiosemicarbazones are formed from A. and semicarbazide or thiosemicarbazide. They too can be used for the purification and characterization of the A.

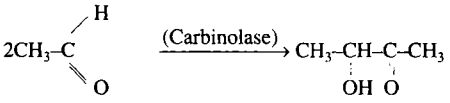
A. with α hydrogen atoms undergo the aldol reaction in the presence of bases or acids to form aldols; when these are subjected to higher temperatures, they split out water to form α,β-unsaturated A.:



Aromatic A. disproportionate under these conditions to the corresponding carboxylic acids and alcohols, in the Cannizzaro reaction (see). In the presence of aluminum alcoholates, this disproportionation also occurs with aliphatic A.

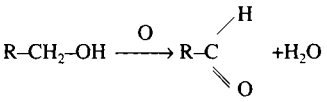
In reactions similar to the aldol reaction, A. can also condense with other CH-acidic reactants, such as malonic acid and its derivatives in the Knoevenagel condensation (see), acetanhydride/sodium acetate in the Perkin reaction (see) and with α-halogencarboxylate esters in the Darzens-Erlenmeyer-Claisen condensation (see).

Many aromatic A. form benzoins in the presence of potassium cyanide or certain thiazolium or imidazolium salts through the benzoin condensation. The structurally analogous aliphatic compounds, the acyloins, can only be obtained directly from aliphatic A. by use of enzymes from certain species of yeast:

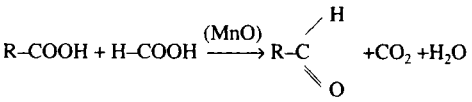


Analytical. A. and ketones can be characterized chemically in the form of derivatives, by IR and NMR spectroscopy, and by mass spectrometric fragmentation. Their IR spectra are characterized by intense bands for the C=O valence vibration in the range of 1680 to 1740 cm^{-1}. The C-H vibrations of A. appear between 2665 and 2880 cm^{-1}. The signals of the aldehyde protons in ^1H NMR spectra are to be expected in the range of $\delta = 9$ to 10 ppm. In ^{13}C NMR, signals in the range of $\delta = 180$ to 210 ppm are very probably due to the C=O groups of A. and ketones. In the mass spectra of aromatic A. and ketones, a characteristic key fragment is the benzoyl cation.

Occurrence and isolation. Various A. are found in low concentrations in plants, especially in numerous etheric oils, e.g. citral, citronellal. For the synthesis of A., there are special methods in addition to the numerous general methods which are also applicable to ketones. The best known and most important method for the synthesis of aliphatic A. is partial oxidation or dehydrogenation of primary alcohols:



Suitable oxidation agents are chromium(VI) oxide or potassium dichromate in sulfuric acid, oxygen in the presence of heated copper or silver, manganese dioxide and selenium dioxide. Another important industrial technique is pyrolysis of mixtures of a carboxylic acid and formic acid in the presence of manganese(II) oxide:



Aliphatic A. can also be produced by cleavage of glycols or hydroformylation of alkenes with carbon monoxide and water in the presence of dicobalto octacarbonyl around 150 °C and pressure of about $3 \cdot 10^4$ kPa. Some other synthetic methods for A. are the Rosenmund reduction (see) of carboxyl chlorides, the Grignard reaction (see) of ortho-formate esters with the Grignard reagent, the Sommelet reaction (see) of alkyl halides with urotropin, the Stephen reduction (see) of nitriles, the Nef reaction (see) of primary nitroalkanes with dilute mineral acids, the Krönke reaction (see) from nitrones, the Vilsmeier-Haack reaction (see) of arenes, the Gattermann synthesis (see) of arenes with hydrogen cyanide and hydrogen chloride in the presence of aluminum chloride and the Gattermann-Koch synthesis (see).

Applications. A. are used mainly as starting materials for numerous syntheses, including industrially important ones, and as perfumes and flavorings in cosmetics and foods. A much broader area is the use of A. as intermediates in the industrial synthesis of styryl and azomethine dyes and many classes of organic compounds, e.g. carboxylic acids, alcohols, nitriles and amines.

Aliphatic and aromatic aldehydes

Formaldehyde	H–CHO
Acetaldehyde	CH_3–CHO
Propionaldehyde	CH_3–CH_2–CHO
Butyraldehyde	CH_2–$(CH_2)_2$–CHO
Acrolein	CH_2=CH–CHO
Crotonaldehyde	CH_3–CH=CH–CHO
Benzaldehyde	C_6H_5–CHO
Cinnamaldehyde	C_6H_5–CH=CH–CHO

Aldehyde carboxylic acids: see Oxocarboxylic acids.

Aldehyde collidines: see Collidines.

Aldehyde group: the functional group, -CHO, of an Aldehyde (see).

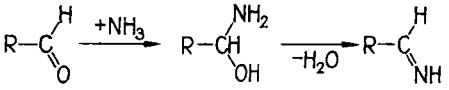
Aldehyde hydrates: addition products of aldehydes and water with the general formula R-CH(OH)$_2$. Most A. are very unstable compounds, because the equilibrium of the addition reaction lies on the side of the reactants. A. are stabilized by strongly electron-withdrawing substituents, e.g. chloral hydrate.

Aldehyde resin: a synthetic resin produced by condensation of aldehydes, especially acetaldehyde, acrolein or furfural. Industrial syntheses in aqueous or alkaline media containing strong alkalies (concentrated sodium or potassium hydroxide) are most common. The first product is a water-sensitive, soft, crude resin; this is converted into an elastic, polishable, thermostable product which is insensitive to strong acids and bases by special treatments. These include exposure to steam or hot air, esterification with glycerol and fusion with other resins (colophony, cumarone-indene resin) or metal hydroxides. Because they are stable to light, have no odor and are not toxic, these products are used for paints and polishes. Acrolein A. have good electrical properties. Condensation of furfural in alkaline media produces dark, alcoholic varnishing resins; in acidic media, furfural condenses to hard rubber substitutes which are highly resistant to alkalies and acids. Rapidly drying varnishes are often based on A.

Aldicarb: see Carbamate insecticides (table); A. is also a nematocide.

Aldimorph: see Morpholine and piperazine fungicides.

Aldimines: Organic compounds with the general formula R-CH=NH. They are formed by the reaction of ammonia with aldehydes, via the unstable aldehyde ammine:



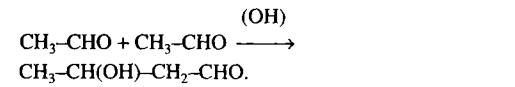
Aldehyde ammine

Alditols, ***sugar alcohols***: reduction products of monosaccharides. The name is formed from the root name for the aldose plus the suffix -itol. Reduction of the sugars is carried out in neutral media, e.g. by amalgams or catalytically. The reduction of a ketose produces a new center of chirality, and thus two isomeric A., for example, glucitol and mannitol from fructose. A. taste sweet and are used as sugar substitutes (see Sweeteners). The best-known A. are *D-glucitol (sorbitol)*, *D-mannitol* and *xylitol*.

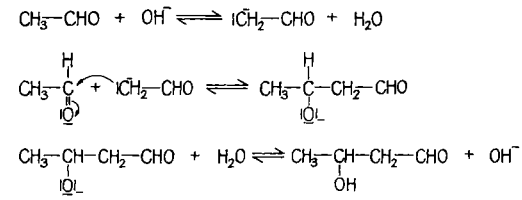
Aldolases: enzymes which catalyse the cleavage of hexose chains into two C_3 units, e.g. fructose 1,6-bisphosphate into D-glyceraldehyde 3-phosphate and dihydroxyacetone phosphate. Examples are ***liver A.*** (M_r 158,000) and ***muscle A.*** (M_r 160,000). The human skeletal musculature contains very high A. activity; the appearance of elevated levels of A. in the serum is diagnostic of certain muscle diseases.

Aldol condensation: same as aldol reaction.

Aldol reaction, ***aldol condensation, aldol addition***: originally, the acid- or base-catalysed dimerization of aliphatic aldehydes with α-hydrogen atoms to form β-hydroxyaldehydes (aldols). For example, under the conditions of A., acetaldehyde is converted to acetaldol:

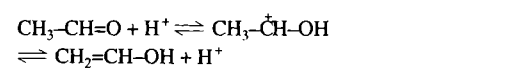


In the general sense, all reactions of ketones and aldehydes with CH-acidic compounds can be considered A., since the reaction mechanism is the same in all cases. The mechanism of A. under basic conditions can be formulated as follows:

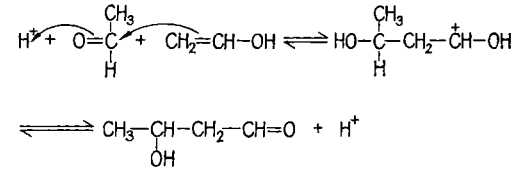


The nucleophilic attack of the carbanion at the carbonyl carbon atom of the aldehyde is the actual aldol addition. The addition product of base-catalysed A. is in many cases stable enough to be isolated.

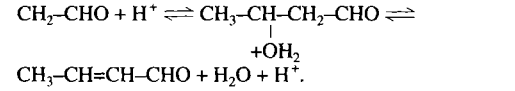
Acid-catalysed A. is initiated by formation of the enol form of the CN-acidic component:



In the further course of the reaction, the basic properties of the C=C double bond of the enol cause the nucleophilic attack on the C atom of the carbonyl group:

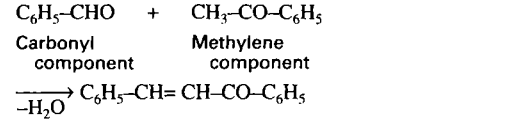


In acid-catalysed A., the addition product cannot be isolated, because under these conditions water is inevitably split off:



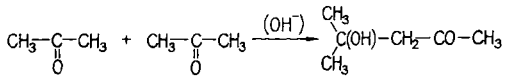
The reaction product is an α,β-unsaturated carbonyl compound, i.e. a product of aldol condensation in the narrow sense of the term. Base catalysis is much more widely used in synthesis than acid catalysis.

Aldehydes which do not have an α-hydrogen atom, e.g. benzaldehyde, cannot undergo A. However, they are able to serve as the carbonyl component in a reaction with other aldehydes or ketones to form the corresponding aldol reaction products:



When aromatic reaction components are used, water is usually split off the addition products, even under basic conditions, leading to α,β-unsaturated carbonyl compounds. The driving force for this reaction step is the formation of a system of conjugated double bonds.

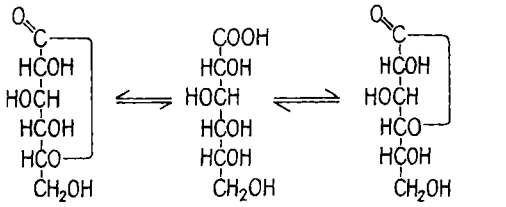
Aliphatic ketones react analogously to the aldehydes, forming β-hydroxyketones, e.g. the A. of acetone produces diacetone alcohol:



In the acid-catalysed reaction, this is dehydrated to mesityl oxide.

If a mixture of an aldehyde and a ketone, each with an α-hydrogen atom and thus capable of A., is subjected to this reaction, the aldehyde always acts as the carbonyl component, due to its higher carbonyl reactivity, and the ketone acts as the methylene component. The reaction product in such cases is always a β-hydroxyketone. Instead of an aldehyde or ketone, other CH-acidic compounds such as malonate esters, cyanoacetate esters, malonic acid dinitrile, acetoacetate esters and aliphatic nitro-compounds, can be used as the methylene component in A. Thus reactions like the Knoevenagel condensation (see), the Perkin reaction (see) or the Darzens-Erlenmeyer-Claisen condensation (see) can be considered special cases of A. The reactivity of the carbonyl components increases in the series: ketones, branched aldehydes, straight-chain aldehydes. The A. is reversible at each step. The addition products can be cleaved into the starting components by acids or bases.

Aldonic acids: monocarboxylic acids formed by oxidation of aldehyde groups on aldoses. If the secondary hydroxyl of an A. is oxidized to a carbonyl group, the product is a ***ketoaldonic acid***. Depending on the number of C-atoms, an A. is classified as an aldotrionic, aldotetronic, aldopentonic, etc. acid. A. are formed by mild oxidation of monosaccharides, e.g. with bromine water. Bacteria and other microorganisms contain glucose oxidases which oxidize D-glucose to ***D-gluconic acid*** (abb. *GlcA*). In free A., nucleophilic attack on the carboxyl group by an hydroxyl group readily leads to formation of a 1,4- or 1,5-lactone. In aqueous solution, the equilibrium lies on the side of the lactone. A. form insoluble salts with alkaline earth metal cations. Both free and bound A. are rare in nature. D-Gluconic acid is used as an additive to soft drinks and as an etching reagent for metals. Its calcium salt is used for calcium therapy. D-Glucono-1,5-lactone is added to sausages. Ascorbic acid is a derivative of an A.



Aldoses: see Monosaccharides.

Aldosterone: see Adrenal cortex hormones.

Aldosterone antagonists: see Diuretics.

Aldoximes: see Oximes.

Aldrin: see Cyclodiene insectides.

Alginates: see Alginic acid.

Alginate fibers: synthetic fibers made by spinning a solution of sodium alginate into a precipitation bath. The sodium alginate solution is made by extraction of alginic acid from dried algae with a sodium carbonate solution. ***Calcium alginate fibers*** are made by spinning the sodium alginate solution into a weakly acidic calcium chloride solution. The A. do not "pill", are not inflammable and are insoluble in organic solvents; however, they are soluble in alkaline aqueous solutions.

In the textile industry, the A. are used as supplemental threads and to achieve special effects. They are used in dentistry as self-dissolving threads.

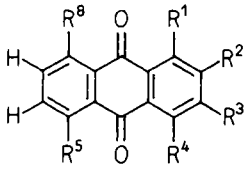
Alginic acid: a linear heteropolysaccharide found in the cell walls of algae, especially brown algae. A. forms a colorless, highly hygroscopic powder. It is only slightly soluble in cold water, but swells strongly; it is insoluble in organic solvents. Stable gels are formed by association of the polyuronide chains of the A. with divalent cations. Salts and esters of A. are called ***alginates***. A. consists of (1→4)-glycosidically linked β-D-mannuronic acid and α-L-guluronic acid esters. It is produced from algae growing on the coasts of the Atlantic and Pacific Oceans, especially *Laminaria* species, *Macrocystis pyrifera, Nereocystis luetkeana, Ascophyllum nodosum* and *Ecklonia maxima*. Up to 40% of the dry mass of the algae can be A. The A. is extracted with sodium carbonate solution and precipitated again with dilute hydrochloric acid. The applications of A. are based on its ability to form gels and to stabilize emulsions. Alginates are used in food, cosmetics and pharmaceuticals as thickeners and protective colloids, and also to make coatings and dental impressions.

Alginite: see Macerals.

Alicyclic: a term for hydrocarbon ring compounds of various sizes which can be visualized as having been formed from aliphatic compounds.

Aliphatic: an adjective applied to hydrocarbon compounds with their carbon atoms arranged in chains (but not containing systems of conjugated double bonds).

Alizarin pigments: a group of synthetic pigments based on the alizarin skeleton. This is modified by addition of reactive groups, such as hydroxyl, amino, nitro and sulfo groups (Table). A. are important mordant dyes; with aluminum or chromium mordants, they make very fast wool dyes, e.g. ***alizarin black S***. *Alizarin*, 1,2-dihydroxy-9,10-anthracenedione occurs in the root of the madder plant, *Rubia tinctorum*, in combination with 2 moles glucose. It was known and used in ancient Egypt, Persia and India.



For key to substituents, see p. 36

Pigment	R^1	R^2	R^3	R^4	R^5	R^8
Alizarin	OH	OH	OH	H	H	H
Alizarinbordeaux	OH	OH	H	H	OH	OH
Purpurin	OH	OH	H	OH	H	H
Alizarin Orange	OH	OH	NO_2	H	H	H
Alizarin Red	OH	OH	SO_3H	H	H	H
Alizarin Saphirol B	NH_2 ($+SO_3H$ in position 7)	H	SO_3H	OH	NH_2	OH

Alizarin violet: same as Gallein (see).

Alkali: a substance which gives alkaline aqueous solutions (see Basic reaction). The most important A. are the hydroxides of sodium and potassium, which are called ***caustic*** A. because of their caustic properties (see Caustification). They have low melting points and a characteristic flavor of lye. In the broad sense, the A. also include the alkaline earth hydroxides and aqueous ammonia. The alkali metal carbonates, such as sodium carbonate (soda), Na_2CO_3, and potassium carbonate (potash), K_2CO_3, are called ***mild A.*** because of their weaker basicity.

Alkali fusion: a method for production of phenols. A. is used mainly for replacement of aromatic sulfur groups by hydroxyl groups, using alkalies.

Alkali metals: the elements lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr), which comprise the 1st main group of the periodic system. The chemical and physical properties of the A. are similar, although there are regular variations within the group. A. are light metals with low melting and boiling points; they can be cut with a knife. They form alloys with each other, some of which are liquid at room temperature. For example, the eutectic Na-K mixture containing 77.2% K melts at - 12.3 °C. The A. are produced by melt electrolysis of their chlorides.

The A. are highly electropositive, in agreement with their electron configuration, and thus their position in the periodic system. Their characteristic electron configuration is a single s-electron outside the filled noble gas shell of the next lower element. As can be seen from the 1st ionization potential, this electron is easily lost; as a result, the A. occur almost without exception in the positive monovalent state. For the same reason, they are also highly reactive, usually as reducing agents. Their standard electrode potentials are so high that the A. occupy the extreme negative end of the electrochemical potential series, and are thus among the strongest known reducing agents, as shown by their reactions with oxygen, hydrogen, water and halogens. The silver sheen of freshly cut surfaces of the A. are rapidly covered, when exposed to moist air, with a dull layer of the oxide or hydroxide. This makes it necessary to keep the A. under inert liquids, usually mineral oil, which prevent access of air. The reactivity of the A. increases markedly from lithium to cesium. This is due to the decreasing coulomb interaction between the nucleus and the outer electron as the atomic radius increases; it is reflected by the decreasing ionization potentials. The A. react with water according to the equation: $2\ M + 2\ H_2O \rightleftarrows 2\ M^+ + 2\ OH^- + H_2$. While lithium reacts slowly at room temperature, potassium usually reacts explosively, igniting the evolved hydrogen. The A. burn in air, lithium to Li_2O, sodium primarily to the peroxide Na_2O_2 and both potassium and rubidium to mixtures of the peroxides and superoxides, K_2O_2 and KO_2, Rb_2O_2 and RbO_2. Since they are very electropositive, the A. react preferentially with the electronegative elements on the right side of the periodic table, forming ionic compounds. Many of these salts have industrial applications. Aqueous solutions of the hydroxides are widely used as strong bases (see Alkali).

The A. dissolve in liquid ammonia to form dark blue solutions which conduct electricity. Both phenomena are due to the presence of electrons solvated by the ammonia. Volatile A. compounds produce characteristic colors in a gas flame which are used for qualitative and quantitative analysis of these elements.

In accordance with the general diagonal relationship in the Periodic system (see), lithium resembles magnesium more closely than it does the other members of the A. The unusually small ionic radius of the Li^+ ion makes it highly polarizing. As a result, Li^+ has a very pronounced tendency to become solvated, and the lattice energies of unsolvated Li salts are high. These effects are responsible for the differences between the solubilities of Li salts and those of heavier homologous compounds, and they explain the similarity to mganesium salts. The polarizing effect of the Li cation is also the reason for a tendency of lithium to form covalent compounds, a tendency not shared by its heavier homologs. This gives lithium its special importance in organoelement chemistry.

The A. are found in nature as various salts. Sodium and potassium make up considerable fractions of the earth's crust, but lithium, rubidium and cesium are relatively rare elements. As a member of natural radioactive decay series, francium occurs in trace amounts in nature (Table).

Properties of the elements of the 1st main group of the periodic system

	Li	Na	K	Rb	Cs	Fr
Nuclear charge	3	11	19	37	55	87
Electronic configuration	[H] $2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe] $6s^1$	[Rn] $7s^1$
Atomic mass	6.941	22.9897	39.0983	85.4678	132.905	(223)
Atomic radius [pm]	134	154	196	211	225	.
Ionic radius [pm]	60	95	133	148	169	.
Electronegativity	0.97	1.01	0.91	0.89	0.86	.
1st ionization potential [eV]	5.392	5.139	4.341	4.177	3.894	.
Standard electrode potential [V]	-3.045	-2.7109	-2.924	-2.925	-2.923	.
Density [g cm^{-3}]	0.534	0.968	0.86	1.532	1.878	.
m.p. [°C]	180.54	97.81	63.65	38.89	28.40	(27)
b.p. [°C]	1317	882.9	774	688	678.4	(677)

Properties of the elements of group IIa of the periodic system

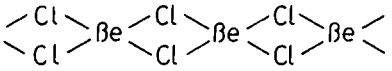
	Be	Mg	Ca	Sr	Ba	Ra
Nuclear charge	4	12	20	38	56	88
Electronic configuration	[He] $2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe] $6s^2$	[Rn] $7s^2$
Atomic mass	9.0122	24.312	40.08	87.62	137.34	226.0254
Atomic radius [pm]	112	160	197	215	222	.
Ionic radius [pm]	31	65	99	113	135	.
Electronegativity	1.47	1.23	1.04	0.99	0.97	(0.97)
1st ionization potential [eV]	9.322	7.646	6.113	5.695	5.212	5.279
2nd ionization potential [eV]	18.211	15.035	11.871	11.030	10.004	10.147
Standard electrode potential [V]	−1.70	−2.375	−2.76	−2.89	−2.90	.
Density [g cm^{-3}]	1.85	1.74	1.54	2.6	3.51	5.50)
m.p. [°C]	1278	648.8	839	769	725	(700)
b.p. [°C]	2970	1107	1484	1384	1640	(1140)

Alkalimetry: a method of Neutralization analysis (see) in which bases are used as standard solutions. However, titration with acid is still occasionally called A., without regard for the usual rules.

Alkaline earth metals: group IIa of the periodic system, including beryllium, magnesium, calcium, strontium, barium and radium. With the exception of radium, the A. are light metals. There is a distinct difference between the properties of calcium, strontium and barium, the A. in the narrower sense, and those of beryllium. The properties of magnesium are intermediate.

The A. are strongly electropositive elements, in accordance with their ns^2 electron configuration and their position in the periodic system. The ionization potentials, especially for the second electron, are considerably higher than those of the alkali metals. However, this energy, which must be expended to form compounds, is more than compensated by the high lattice energies of solid salts and by the high solvation enthalpies of the divalent cations in solutions. These considerations apply to magnesium, calcium, strontium and barium, and explain why these elements always have the +2 oxidation state in their stable compounds; they also explain the high reducing capacity of these metals, which is reflected by their high standard electrode potentials.

The unusually small atomic and ionic radii of beryllium, which lead to very high ionization potentials, make it impossible for Be to form divalent cations. Instead, it forms two covalent bonds which, however, only complete an electron quartet. This electron-deficient situation accounts for the Lewis acidity of many Be compounds, and is often compensated by polymerization. For example, solid beryllium chloride, $BeCl_2$, consists of long chains in which the individual Be atoms are linked by two chlorine bridges.



Thus with a coordination number of 4, each Be atom achieves a noble gas configuration. On the whole, beryllium resembles aluminum more than it does magnesium (diagonal relationship in the Periodic system (see)). However, magnesium also has a recognizable tendency to form covalent bonds; because it is able to form stable bonds to carbon, organomagnesium compounds (see Grignard compounds) are important in organic and organometallic syntheses.

As expected, the reactivity of the A. increases with increasing atomic mass. Although calcium, strontium and barium react vigorously with water to form the hydroxides and evolve hydrogen, magnesium is attacked only by hot water, and the reaction is slow. Beryllium is passivated by an oxide skin, and does not react with water. The stability in air also decreases with increasing atomic mass. At high temperatures, the A. react with oxygen to form the oxides (e.g. MgO, CaO). Barium forms the peroxide above 500 °C; this decomposes reversibly at 700 °C:

$$2\ BaO + O_2 \underset{700°C}{\overset{500°C}{\rightleftharpoons}} BaO_2.$$

The strong reducing effect of the A. is utilized in the production of other metals, such as titanium, uranium, and even potassium. The basic character of their hydroxides and oxides increases with increasing atomic mass. Although beryllium hydroxide, $Be(OH)_2$, is amphoteric, barium hydroxide, $Ba(OH)_2$, is a strong base. This trend is related to the increase in decomposition temperatures of A. carbonates (e.g. $CaCO_3 \rightarrow CaO + CO_2$) on going from magnesium to barium. Many A. salts are insoluble in water, and their precipitation is used to detect the presence of the elements. The solubilities of the hydroxides and oxides increase with increasing atomic mass, while those of the carbonates, sulfates and chromates decrease in the same order.

Magnesium (1.9%) and calcium (3.4%) make up significant fractions of the earth's crust. Beryllium is a rare element. The A. occur naturally as carbonates, sulfates, silicates and chlorides in many minerals. Radium occurs as a product of natural radioactive decay of uranium in uranium minerals. The A. are generally produced by melt electrolysis of their chlorides.

Alkaline zinc-manganese dioxide cell: an Electrochemical current source (see) which is an improved version of the Leclanché cell (see). The electrolyte is a 45 to 50% potassium hydroxide solution saturated with zinc oxide. The anode is formed by a zinc powder with a large surface area; this gives a higher energy density, higher capacity and better storage properties.

Alkaloids: biogenic, nitrogen-containing com-

Alkaloids

The most important groups of alkaloids

Chemical group	Parent compound	Examples	Occurrence
Pyrrolidine A.	Pyrrolidine	Hygrin	*Erythroxylaceae (Erythroxylon)*
Indole A.	Pyrrolidinoindole	Physostigmine	*Fabaceae (Physostigma)*
	β-Carboline	Rauwolfia A. (reserpine, ajmaline)	*Apocynaceae (Rauwolfia)*
		Yohimbine	*Rubiaceae (Pausinystalia)*
		Vinca A. (vinblastine, vincristine)	*Apicynaceae (Vinca, Catharanthus)*
	Carbozole	Strychnose A. (strychnine, brucine, calebash curare A.)	*Loganiaceae (Strychnos)*
		Aspidosperma A.	*Apocynaceae (Aspidosperma, Vinca Pleiocarpa)*
		Catharanthus A.	*Apocynaceae (Catharanthus)*
	Ergoline	Ergot A.	Fungus *(Claviceps)*
Pyrrolizidine A.	Pyrrolizidine	Senecio A.	*Asteraceae (Senecio)*
Piperidine A.	Piperidine	Piperine	*Piperaceae (Piper)*
		Coniine	*Apiaceae (Conium)*
		Lobelia A. (lobelin)	*Campanulaceae (Lobelia)*
		Areca A.	*Palmae (Areca)*
	Tropane	Hyoscyamine, scopolamine, atropine	*Solanaceae (Atropa, Datura, Hyoscyamus, Scopolia)*
		Cocaine	*Erythroxylaceae (Erythroxylon)*
Quinolizidine A.	Quinolizidine	Sparteine, cytisine, lupinine	*Fabaceae (Lupinus, Cytisius, Genista)*
Pyridine A.	Pyridine	Nicotine	*Solanaceae (Nicotiniana)*
Quinoline A.	Quinoline	Quina A. (quinine, quininidine)	*Rubiaceae (Cinchona)*
Isoquinoline A.	Isoquinoline	Anhalonium A.	*Cactaceae (Anhalonium)*
	Benzylisoquinoline	Opium A. (papaverine)	*Papaveraceae (Papaver)*
	Bisbenzylisoquinoline		*Annonaceae, Berberidaceae, Hernandiaceae, Lauraceae, Magnoliaceae, Monimaceae, Nymphaceae, Ranunculaceae*
		Tubocurarine	*Menispermaceae (Chondrodendron)*
	Phthalidisoquinoline	Opium A. (narcotine)	*Berberidaceae (Berberis)*
		Narcotine	*Papaveraceae (Papaver)*
	Aporphine	Apomorphine	
	Morphinane	Opium A. (morphine, codeine, thebaine)	*Papaveraceae (Papaver)*
	Benzoquinazoline	Ipecacuanha A. (emetine)	*Rubiaceae (Cephalis)*

Typical alkaloid reagents

Reagent	Composition	Reaction
Mayer's	$K_2[HgI_4]$	Yellowish-white precipitate
Dragendorff's	$K[BiI_4]$	Orange precipitate
Sonnenschein's	Phosphomolybdanic acid	Yellow precipitate which turns blue-green
Scheibler's	Phosphotungstic acid	Precipitate
Wagner's	KI_3	Brown precipitate
Erdmann's	HNO_3/H_2SO_4	Coloration
Fröhde's	Molybdanic acid/H_2SO_4	Coloration
Marquis'	Formaldehyde/H_2SO_4	Violet color (opium A.)

pounds. Most are N-heterocyclic. Amino acids, peptides, nucleosides, amino sugars and antibiotics are not considered A.

Classification. A. are classified according to their structures or their origins (Table). The largest groups are the indole and isoquinoline A., and these two groups also include numerous ***dimeric A. (bisalkaloids***). The pseudo- and protoalkaloids are distinguished from these ***A. in the narrow sense***. ***Pseudoalkaloids*** are compounds whose basic carbon skeletons are not derived from amino acids, including, for example, the steroid alkaloids and coniine. ***Protoalkaloids*** are compounds in which the N atom derived from an amino acid is not part of the heterocycle; this group includes the Biogenic amines (see).

Occurrence. A. are most abundant in higher plants, especially the *Magnoliatae*, and less commonly in the *Liliatae* or *Pinidae*. The families *Apocynaceae, Buxaceae, Asteraceae, Euphorbiaceae, Loganiaceae, Menispermaceae, Papaveraceae, Rutaceae* and *Solanaceae* are especially rich in A. Usually a plant contains a primary A. and numerous secondary A., which differ with respect to methylation or hydrogenation. About 20% of higher plants contain A. They are found in some non-spermatophytes, including club mosses, horse-tails and fungi (e.g. ergot). A. are also found sporadically in animals, such as salamanders, toads (indolylalkylamines), frogs (batrachotoxin, pumiliotoxins), fish (tetrodotoxin) and millipedes (quinazoline derivatives).

Properties and determination. With a few exceptions, in which the N atom is acylated (e.g. colchicine), the A. are basic. The basicity depends on the heterocyclic skeleton and its substituents. Some A. bases, e.g. nicotine, hygrine and sparteine, are liquids, but most A. crystallize. The free bases, most of which are colorless, are only slightly soluble in water but are more readily soluble in organic solvents. The salts of A. are soluble in water, and they are used therapeutically in this form. The A. are determined by precipitation with picric acid or the reagents listed in the table, or by more or less group-specific color reactions. They are tested for purity mainly by thin-layer chromatography.

Isolation. A. are found in plants as salts of organic or inorganic acids. The A. is isolated from the plant material by treating it with alkali; the free alkaloid base is then extracted with organic solvents, or, more rarely, by steam distillation. The extracted A. are usually mixtures, which are then separated by fractional crystallization of suitable salts (e.g. hydrohalides, perchlorates, picrates or oxalates) or by chromatography.

Biosynthesis. Incorporation of radioactively labelled amino acids has demonstrated that nearly all A. are synthesized from the amino acids phenylalanine (isoquinoline A.), tryptophan (indole A.), lysine (piperidine A.) or proline or ornithine (pyrrolidine A.). A. can also contain isoprenoid components; examples are the steroid A. and some indole A.

Applications. Many A. are biologically active. Plants containing A. have therefore long been used in medicine. Today, pure A. are usually used instead of the plant preparations. Some of the most important are morphine and its derivatives (as analgesics), papaverine (as a spasmolytic), curare A. (as muscle relaxants), rauwolfia A. (as antihypertonics and neuroleptics), quinine (against malaria), catharanthus A. (as a cytostatic), quinidine and ajmaline (as antiarrhythmics) and cocaine (as a local anaesthetic, and as an illicit drug). Many pharmaceuticals were modelled on A. A few A. are used as pesticides (e.g., nicotine).

Alkanals: saturated aliphatic Aldehydes (see).

Alkanes, ***paraffins***: aliphatic hydrocarbons with the general formula C_nH_{2n+1}. A. contain exclusively sp^3-hybridized C atoms which are saturated with hydrogen.

The A. constitute a homologous series of compounds in which two neighboring members of the series differ by one $-CH_2-$ group (Table 1). The compounds are chemically similar, and their physical properties change in a continuous manner along the series.

Table 1. Homologous series of alkanes

Methane	CH_4	Decane	$C_{10}H_{22}$
Ethane	CH_3-CH_3	Undecane	$C_{11}H_{24}$
Propane	$CH_3-CH_2-CH_3$	Dodecane	$C_{12}H_{26}$
Butane	$CH_3-(CH_2)_2-CH_3$	Tridecane	$C_{13}H_{28}$
Pentane	$CH_3-(CH_2)_3-CH_3$	Tetradecane	$C_{14}H_{30}$
Hexane	$CH_3-(CH_2)_4-CH_3$	Pentadecane	$C_{15}H_{32}$
Heptane	$CH_3-(CH_2)_5-CH_3$	Eicosane	$C_{20}H_{42}$
Octane	$CH_3-(CH_2)_6-CH_3$	Triacontane	$C_{30}H_{62}$
Nonane	$CH_3-(CH_2)_7-CH_3$	Tetracontane	$C_{40}H_{82}$

Beginning with butane, C_4H_{10}, there are isomers of each compound; the number of isomers increases with the number of carbon atoms. A distinction is made between *linear* and *branched* A. From C_7H_{16} on, some of the isomers contain asymmetric carbon atoms, so there are stereoisomers in addition to structural isomers (Table 2). The rules for naming A. are given under Nomenclature (see), sect. III C.

Properties. The first four A. of the homologous series are gases, The next members of the series, up to C_{16}, are liquids, and the compounds from C_{17} on are solids. The boiling points of branched A. are lower than those of the isomeric *n*-A. The boiling points of the higher members of the series are closer together, making separation by distillation more difficult.

Table 2. Number of isomeric alkanes

No. of C atoms	Name of compound	No. of structural isomers	No. of structural and stereoisomers
1	Methane	1	1
2	Ethane	1	1
3	Propane	1	1
4	Butane	2	2
5	Pentane	3	3
6	Hexane	5	5
7	Heptane	9	11
8	Octane	18	24
9	Nonane	35	55
10	Decane	75	136
20	Eicosane	366 319	3 395 964

The gaseous and solid A. have no odor, and the liquids usually have a typical gasoline smell. The A. are not miscible with water; they dissolve in ether and

ethanol, but their solubility decreases with increasing molar mass. A. are combustible, and the gaseous and liquid compounds are more readily ignited than their higher homologs. The lower compounds also form explosive mixtures with air. Complete combustion produces carbon dioxide and water, while incomplete combustion also produces carbon monoxide and/or soot. Although the reactivity of A. is low, relative to many other classes of compounds, most will undergo radical reactions under appropriate conditions, and these are utilized industrially. The branched A. are generally more reactive than *n*-A.

Natural occurrence. A. are found in natural gas and petroleum deposits, and their extraction and use are major contributors to the world economy. Petrochemical methods are used to produce both pure A. and various fractions of A. mixtures.

Production. A. are usually produced from natural gas, petroleum or, especially in countries with large coal deposits, by liquefaction of coal. The following methods of synthesis are suitable for laboratory purposes:

1) Catalytic hydrogenation of alkenes and alkynes:

$$R^1\text{–}C{\equiv}C\text{–}R^2 + H_2 \longrightarrow R^1\text{–}CH{=}CH\text{–}R^2$$

$$\xrightarrow{+H_2} R^1\text{–}CH_2\text{–}CH_2\text{–}R^2$$

Platinum, palladium or finely divided nickel can be used as catalyst.

2) Reduction of alcohols or alkyl iodides with hydrogen iodide: R-OH + HI → R-I + H_2O; R-I + HI → R-H + I_2. It is convenient to carry out the reaction with a mixture of hydrogen iodide and red phosphorus, so that the hydrogen iodide is regenerated: 2 P + 3 I_2 → 2 PI_3; 2 PI_3 + 6 H_2O → 2 $P(OH)_3$ + 6 HI.

3) Hydrolysis of Grignard compounds: R-X + Mg → RMgX (X = Cl, Br, I); RMgX + H_2O → R-H + Mg(OH)X.

4) Reaction of alkyl halides with sodium (see Wurtz reaction).

5) Electrolysis of the alkali salts of carboxylic acids in aqueous solutions (see Kolbe synthesis), which, like the Wurtz reaction, is suitable for synthesis of long-chain A.

6) Aldehydes and ketones can be converted to A. by the Wolff-Kishner reduction (see) of hydrazone, or by direct reduction with zinc amalgam (see Clemmensen reduction).

The typical reactions of A. are radical substitutions. For example, at high temperatures and in the presence of UV light, chlorine can react with methane in the gas phase to produce chloromethane, dichloromethane, chloroform and carbon tetrachloride:

$$CH_4 + Cl_2 \rightarrow CH_3Cl/CH_2Cl_2/CHCl_3/CCl_4.$$

By suitable choice of reaction conditions and reactant concentrations, the relative yields of the products can be manipulated as desired; they can also be separated by fractional distillation.

Under similar conditions, a mixture of chlorine and sulfur dioxide produces sulfonyl chlorides:

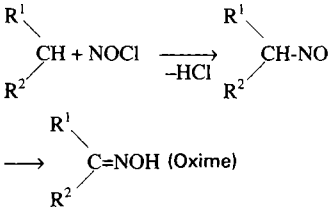
$$Cl_2 \rightarrow 2\ Cl\cdot$$
$$R\text{-}H + Cl\cdot \rightarrow R\cdot + H\text{-}Cl$$
$$R\cdot + SO_2 \rightarrow R\text{-}SO_2\cdot$$
$$R\text{-}CO_2\cdot + Cl_2 \rightarrow R\text{-}CO_2Cl + Cl\cdot$$

Alkane sulfonyl chloride

The end products of this radical chain reaction, which is used industrially with long-chain A., are valuable intermediates for production of detergents. Sulfoxidation with sulfur dioxide and oxygen produces mixtures of alkane sulfonic acids: 2 R-H + SO_2 + O_2 → 2 R-SO_3H (alkane sulfonic acid). Nitration of A. in the gas phase at 400 °C with nitric acid yields mixtures of isomeric nitroalkanes; partial oxidative cleavage of these gives lower nitroalkanes as well:

$$CH_3\text{–}CH_2\text{–}CH_3 \longrightarrow CH_3\text{–}CH_2\text{–}CH_2\text{–}NO_2/CH_3\text{–}\underset{\displaystyle NO_2}{\underset{|}{CH}}\text{–}CH_3$$

(1-nitropropane/2-nitropropane) and CH_3-CH_2-NO_2/CH_3-NO_2 (nitroethane/nitromethane). Nitration with nitrosyl chloride, NOCl, yields nitrosoalkanes, which can be rearranged to oximes:



Such reactions are important in the production of polyamides by subsequent Beckmann rearrangements. The oxidation of A. in excess air or oxygen produces CO_2 and H_2O; incomplete combustion also produces CO or soot. The latter reaction is carried out under controlled conditions with methane, to produce soot used as filler material for tires. Controlled oxidations can also be carried out in such a way that C-C cleavage produces lower or medium-length carboxylic acids (see Paraffin oxidation).

Recently, ionic reactions of A. have become more significant; these include rearrangements and isomerizations such as the conversion of butane to isobutane when heated with aluminum(III) chloride and alkenes. Reactions which might permit a rapid identification of A. by formation of derivatives are not known. They must therefore be characterized on the basis of their physical constants and spectral data. Mixtures are usually separated, and the individual components are identified by combination of gas chromatography and mass spectroscopy.

A. are used as heating gases, e.g. natural gas (methane), propane and butane; the liquid A. C_5 to C_{16} are used as fuel in internal combustion engines, diesel engines, furnaces and as lubricants. Because they can form explosive mixtures with air or oxygen, the A. up to about C_{10} must be handled with caution. However, their use as fuels for engines depends precisely on this property. Branched A. are especially important for production of an even combustion with-

out residues or "knocking" of the engine (see Octane rating). Pure A. of various chain lengths, e.g. pentane or hexane, are used as solvents. The semisolid and solid mixtures of compounds containing more than 16 or 17 C atoms are used as vaseline, soft and hard paraffins, pharmaceutical preparations, paraffin packings in medicine, and for candles.

Alkane sulfonates, also ***secondary A.***, abb. ***SAS***: an economically important group of anionic Surfactants (see); a mixture of isomers and homologs R^1-$HC(SO_3Na)$-R^2 (where R^1, R^2 = C_{11} to C_{17}) formed by sulfoxidation or sulfochlorination of alkanes and subsequent neutralization or saponification of the sulfochlorides by sodium hydroxide. A. are biodegradable, and are used mainly as detergents for washing dishes, clothes and household cleaning; they are also used to some extent in personal hygiene products, in emulsion polymerization reactions and in fire extinguishers. A. are very stable to hydrolysis, and can therefore also be used in acidic or alkaline cleansers. They can also be incorporated into powdered laundry products.

Alkane sulfonic acids: see Sulfonic acids.

Alkannin, ***alkanna, alkanna red***: a dark red to yellowish red natural pigment, m.p. 149 °C. A. can be extracted from the roots of *Lawsonia alba* or *L. inermis*, or from *Alcanna tinctoria*; it was formerly used in small amounts as a textile dye. ***Alkanna paper*** or ***Böttger's paper*** is an indicator impregnated with an alcoholic solution of A.; it is turned green to blue by bases.

Alkanols: monoalcohols derived from alkanes with the general formula $C_nH_{2n+1}OH$, for example, methanol and ethanol (see Alcohols).

Alkanones: saturated aliphatic Ketones (see).

Alkazide process, same as Sulfosolvane process (see).

Alkenes, ***olefins, ethylene hydrocarbons***: unsaturated hydrocarbons, that is, those containing C-C double bonds. In the broad sense, A. include compounds with one, two or several double bonds. When two or more double bonds are adjacent to each other, they are called cumulative double bonds (C=C=C), and the compound is a Cumulene (see); when two or more double bonds alternate with single bonds (C=C-C=C), they are conjugated (see Dienes or Polyenes). Isolated double bonds are separated by two or more single bonds (C=C-C-C=C).

A. in the narrow sense, simple A., contain only one double bond. These compounds form a homologous series with the general formula C_nH_{2n}, beginning with ethene (Table). Structural and configuration isomers are possible, starting with butene.

Homologous series of alkenes

Ethene	$CH_2=CH_2$
Propene	$CH_2=CH-CH_3$
But-1-ene	$CH_2=CH-CH_2-CH_3$
But-2-ene	$CH_2-CH=CH-CH_3$
Isobutene, 2-methylprop-1-ene	$(CH_3)_2C=CH_2$
Pent-1-ene	$CH_2=CH-CH_2-CH_2-CH_3$
Hex-1-ene	$CH_2=CH-CH_2-CH_2-CH_2-CH_3$

The rules for naming A. are found under Nomenclature (see), sect III C.

Properties. The physical properties of A. are very similar to those of the analogous alkanes. In the homologous series, there are gaseous (C_2 to C_4), liquid (C_5 to C_{17}) and solid compounds. In pairs of E,Z-isomers, the E-diastereomer usually has a higher melting point, a lower boiling point and a lower index of refraction than the Z-diastereomer.

A. are only slightly soluble in water, but dissolve in ether and ethanol. They are combustible, and generally burn to carbon dioxide and water; under oxygen-deficient conditions, carbon monoxide and soot are also produced.

Unlike the alkanes, A. are extremely reactive. The typical reactions are *additions*, because the chemical behavior of the A. is determined mainly by the π-bond with its relatively low π-bonding energy. Since the C=C double bond is nucleophilic, electrophilic reactions occur in addition to radical additions. 1) Catalytic hydrogenation to alkanes in the presence of platinum or palladium catalysts generally occurs at room temperature and normal pressure, or at a slight overpressure (in the laboratory); in industry, elevated temperatures and higher pressures are used:

$$R-CH=CH-R + H_2 \xrightarrow{\text{cat.}} R-CH_2-CH_2-R.$$

This reaction is used both for synthesis of saturated compounds from unsaturated compounds and for quantitative determination of the number of double bonds in the molecules.

2) Addition of halogens usually occurs in the sense of a *trans*-addition, at room temperature; 1,2-adducts are formed: R-CH=CH-R + Br_2 → R-CH(Br)-CH(Br)-R. This reaction is especially significant as a qualitative test for a C=C double bond, e.g. by decoloration of a dilute bromine solution when it is added, dropwise, to a sample solution. It is also used for quantitative determination of the number of double bonds in the molecule, e.g. in determination of the iodine number of fats (addition of iodine to the double bonds in the fat molecules). The decoloration is due to the formation of nearly colorless 1,2-adducts, consuming the bromine or iodine. An excess of iodine can also be used, and the iodine not consumed can then be determined quantitatively by iodometric titration.

3) Addition of hydrogen halides produces halogenated alkanes: $CH_2=CH_2$ + HBr → CH_3-CH_2-Br. The reactivity of the A. towards hydrogen halides increases with increasing acidity: HF < HCl < HBr < HI. In unsymmetrically substituted A., the electrophilic addition occurs regioselectively according to Markovnikov's rule: the electronegative halogen atom is added to the more hydrogen-poor C atom: $CH_3-CH=CH_2$ + HBr → $CH_3-CH(Br)-CH_3$ (2-bromopropane; Markovnikov product). If peroxides are added to the mixture, the reaction can occur as a radical addition according the Kharasch; here the anti-Markovnikov product is favored, e.g. 1-bromopropane from propene:

$$CH_2-CH=CH_2 + HBr \longrightarrow CH_2-CH_2-CH_2-Br$$

(1-Bromopropane; anti-Markovnikov product).

4) Hydration, that is, addition of water to form an alcohol, is the reverse of formation of A. from alcohols (dehydration). It is catalysed by acids, follows the Markovnikov rule, and is industrially important, for example, for production of *tert.*-butanol (see Butanols). When sulfuric acid is used, it is added first, forming acidic sulfate esters; the sodium salts of these esters are used as detergents (see Surfactants). Hydrolysis of the alkyl sulfates also produces alcohols, e.g.:

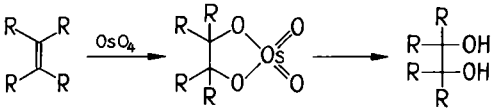
$$CH_3\text{–}CH{=}CH_2 + H_2SO_4 \rightarrow (CH_3)_2CH\text{–}O\text{–}SO_3H \xrightarrow{+H_2O} CH_3\text{–}CH(OH)\text{–}CH_3 + H_2SO_4.$$

On the other hand, alkyl sulfates can react readily with an excess of alcohol to form ethers.

5) Hydroxylation to *cis*-1,2-diols (glycols) can be done with a dilute alkaline solution of potassium permanganate, which is bleached and precipitates as manganese dioxide. This reaction can be used to detect the A. double bond (Baeyer's test):

$$R\text{–}CH{=}CH\text{–}R \xrightarrow{KMnO_2/H_2O} R\text{–}CH(OH)\text{–}CH(OH)\text{–}R + MnO_2.$$

A. can also be hydroxylated on laboratory scale using osmium(VIII) oxide or the less toxic ruthenium(VIII) oxide. This reaction is an addition in the presence of water and the oxidizing agent; glycol esters of manganic, osmic or ruthenic acids are formed as intermediates and then hydrolysed:



6) Epoxidizing is an addition of oxygen to a double bond which produces an Epoxide (see):

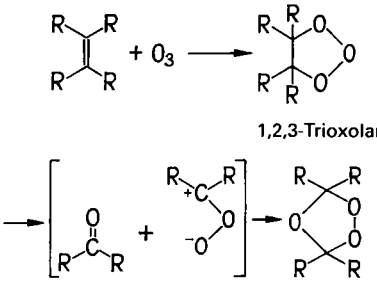
$$CH_2{=}CH_2 \xrightarrow{+O(Ag_2O)} H_2C\text{–}CH_2 \quad (\text{O bridges the two C})$$

For example, the reaction of ethene with silver oxide yields ethylene oxide (oxirane). Some other possible reagents are the per-acids, such as perbenzoic and monoperphthalic acids, or hydroperoxides in the presence of molybdenum and tungsten catalysts. Oxiranes can be converted to *trans*-1,2-diols by acid-catalysed ring opening.

7) Carbonylation is the reaction of A. with carbon monoxide and water in the presence of tetracarbonylnickel at 250 °C and 20 MPa pressure to form carboxylic acids. Acid catalysts can also be used, under different reaction conditions:

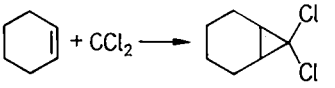
$$CH_3\text{–}CH{=}CH_2 + CO + H_2O \xrightarrow{cat.} (CH_3)_2CH\text{–}COOH.$$

8) Ozonization is a reaction initiated by ozone addition; it leads via a primary ozonide (1,2,3-trioxolane) to a secondary ozonide (1,2,4-trioxolane):



Both ozonides are formed by 1,3-dipolar cycloaddition. In general, the more stable secondary ozonides are cleaved by reduction with zinc and acetic acid, or by catalytic hydrogenation, forming aldehydes and/or ketones (depending on the substitution). In this way, the aldehydes/ketones can be obtained synthetically, or the reaction can be used to determine the position of a double bond in a molecule. It must be kept in mind that ozonides tend to decompose explosively.

9) Carbene transfer is an addition of the carbene to the A. double bond, forming a cyclopropane derivative, as in a Simmons-Smith reaction. 1,1-Dichlorocarbene is easily made from chloroform, and can be added, e.g. to cyclohexene:



In addition to the simple addition reactions, A. tend to *polymerize*, that is, to undergo *polyaddition* of many molecules (monomers) to form macromolecules (polymers):

$$n\ CH_2{=}CH_2 \rightarrow \{CH_2\text{–}CH_2\}_n$$

Ethylene Polyethylene

Polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrene, polyacrylonitrile, polyacrylic esters, etc., are industrially very important. The wide variety of synthetic polymers of A. and substituted A. indicate the significance and applications of simple compounds with A. double bonds.

A. also undergo an extraordinary number of substitution reactions (*allyl substitutions*) under radical conditions. For example, at 400 to 600 °C, propene and chlorine form allyl chloride: $CH_2{=}CH\text{-}CH_3 + Cl_2 \rightarrow CH_2{=}CH\text{-}CH_2\text{-}Cl + HCl$. The reaction with *N*-bromosuccinimide in the presence of peroxides or UV light (see Wohl-Ziegler reaction) is an example of an allyl substitution.

Analytical. Double bonds are detected using alkaline permanganate solution (Baeyer's test) or bromine solution in chloroform; both reagents are bleached on reaction with a double bond. A. form yellow charge-transfer complexes with tetranitromethane. Hydroxylation of the double bond, followed by cleavage of the glycol and ozonolysis, is used to elucidate structure. IR spectra of A. are

characterized by strong bands in the region of C=C valence vibrations between 1620 and 1680 cm^{-1}; the C-H valence vibrations are seen between 3010 and 3095 cm^{-1}. E and Z-isomers have different C-H deformation vibrations: E at 960 to 980 cm^{-1}, Z at 650 to 720 cm^{-1}. A. absorb in the UV between 180 and 200 nm. In ^1H NMR, the signals for olefinic proteins are found at δ = 4.3 to 6 ppm, and are unique to this group. E and Z configuration can often be easily determined from the vicinal coupling constants J: J_Z = 5 to 16 Hz, while J_E = 13 to 21 Hz. The mass spectroscopic fragmentation of A. is characterized by allyl cleavage of the molecular ion; the resulting allyl cations are resonance stabilized. The position of the C=C double bond cannot be determined by mass spectroscopy.

Synthesis. Lower A. (C_2 to C_5) are isolated on the industrial scale from the refinery gases from petroleum processing. They are also made by catalytic dehydrogenation of alkanes or pyrolysis of gasoline or kerosene at 800 to 900 °C. In addition, there are many characteristic methods of synthesis for the laboratory scale or for scientific purposes: 1) dehydration of alcohols by heating with sulfuric or phosphoric acid or zinc chloride:

$$CH_3{-}CH_2{-}CH(OH){-}CH_3 \xrightarrow[-H_2O]{} CH_3{-}CH{=}CH{-}CH_3.$$

A more efficient method is catalytic dehydration on aluminum oxide or thorium oxide catalysts in the gas phase; the competing reactions, such as formation of ethers, are largely suppressed by this method.

2) Dehydrohalogenation of haloalkanes with bases: CH_3-CH_2-Br + KOH → CH_2=CH_2 + KBr + H_2O.

3) Dehalogenation of 1,2-dihaloalkanes by zinc, sodium iodide in methanol, chromium(II) salts or sodium thiosulfate in dimethylsulfoxide:

$$R{-}CH(Br){-}CH(Br){-}R \xrightarrow[-ZnBr_2]{+Zn} R{-}CH{=}CH{-}R.$$

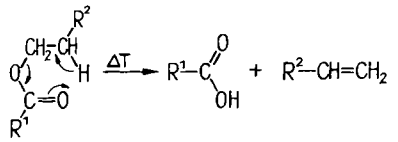
4) Introduction of a double bond by Hoffmann degradation of quarternary ammonium hydroxides.

5) Introduction of a double bond by the Cope reaction, starting from *tert.*-amine oxides.

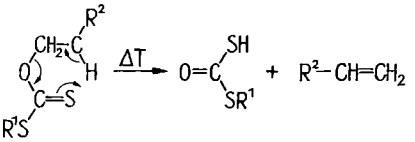
6) Reaction of aldehydes or ketones with alkylide phosphoranes in the sense of the Wittig reaction.

7) Reductive coupling of aldehydes or ketones by treatment with lithium aluminum hydride: 2 $(R)_2C{=}O \rightarrow (R)_2C{=}C(R)_2$.

8) Pyrolysis of carboxylic acid esters at temperatures around 500 °C, leading to synchronous *cis*-elimination:



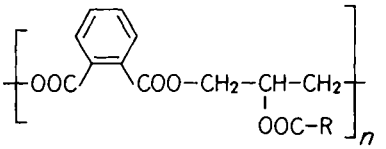
9) Pyrolysis of xanthogenic acid esters (Čugaev reaction) around 200 °C also leads to synchronous *cis*-elimination:



The applications of A. result from their numerous reactions. A. obtained on a large industrial scale from petroleum are used mainly to make highly branched alkanes, alcohols, ethers, epoxides, glycols, carboxylic acids, halogen alkanes, alkyl benzenes, alkyl sulfates and synthetic polymers.

Alkoxide: same as alcoholate (see).

Alkyde resins: synthetic polyester resins made by polymerization of polyvalent alcohols (e.g. glycerol, glycol or pentaerythritol) with dicarboxylic acids (e.g. phthalic, adipic, succinic, maleic acids or their anhydrides). A. with phthalic or maleic acids are called ***phthalate*** and ***malate resins***, respectively, while those consisting of glycerol and phthalic acid are called ***glyptal resins***.



A. can be modified by incorporation of further molecular groups, for example, by esterification of the secondary hydroxyl group of glycerol; such modified A. form elastic films with good binding qualities. 1) Fatty-acid-modified A. are made from the first runnings from paraffin oxidation, the acids of tall oil or unsaponified fats which, when heated with glycerol and phthalic anhydride, are transesterified. 2) Oil-modified A. (oil alkydes) are obtained by heating phthalic anhydride and glycerol with linoleic or ricinoleic acid, or with oils such as wood or poppyseed oil. 3) Resin-modified A. (resin alkydes) are made by incorporation of colophony or copal; abietic acid or copalic acid acts as the esterifying component. 4) Phenalkydes are A. combined with phenol derivatives, and 5) styrolized A. are combinations of styrene and A.

The large selection of polyvalent alcohols, saturated and unsaturated aliphatic and aromatic dicarboxylic acids as starting materials, and the various types of modification give a wide spectrum of variations. There are a few hardening A., but in general they are thermoplastic and soluble in organic solvents. They are used mainly as paint bases which combine well with other components; drying agents such as lead, manganese or cobalt salts of fatty or resin acids are added to the products containing A. based on unsaturated dicarboxylic acids. About 60% of the synthetic paint bases are related to A. A. are also used to make printer's inks, glues, insulation, plastics, floorings and textile treatments.

Alkyde resin varnishes: see Varnish.

Alkyl-: term indicating an atomic group C_nH_{2n+1}, either as a group R in the systematic terminology of compounds, or as an unstable free radical or carbenium ion. A. is derived from "alkane".

Alkyl aluminum compounds: see Organoaluminum compounds.

Alkylated gasoline: see Gasoline.

Alkylating agents: compounds which attack the nucleophilic centers of compounds and alkylate them (see Alkylation). Those which attack biological molecules under physiological conditions are particularly significant. The attack of N atoms in nucleotide bases in nucleic acids, especially the N7 atom of guanine, by di- and trifunctional A. leads to cross-linking of DNA. The A. include mustard gas derivatives, such as chlorambucil and cyclophosphamide, aziridine derivatives, (e.g. thio-tepa), aliphatic sulfonates (e.g. busulfane, CH_3-SO_2-O-$(CH_2)_4$-O-SO_2-CH_3) and certain oxiranes. A. are used as cytostatics and immunosuppressives; they are also mutagenic.

Alkylation: introduction of alkyl groups such as methyl (CH_3-), ethyl (C_2H_5-), etc., into an organic compound. Some well-known alkylating reagents are dialkyl sulfates and haloalkanes, which react preferentially with CH-, NH- and OH-acidic compounds in the presence of bases. For example, alkynes, 1,3-dicarbonyl compounds, amines, nitrogen heterocycles, phenols and enols are readily alkylated. In industry, alkylations of arenes and alkanes under Friedel-Crafts conditions are also very important, e.g. for production of high-octane gasolines. Here alkenes, which are cheaper, are usually used instead of haloalkanes.

Alkylbenzenes: aliphatic-aromatic hydrocarbons in which H atoms on the benzene ring are replaced by alkyl groups, as in toluene or xylene. A. with longer carbon chains are required for the production of alkylbenzene sulfonates, which are used as detergents, e.g. dodecylbenzene or tetradecylbenzene. These A. are produced by Friedel-Crafts reactions from benzene and haloalkanes with 8 to 18 carbon atoms. In technical syntheses, the alkene byproducts from petroleum refining can be used instead of the haloalkanes.

Alkylbenzene sulfonates, abb. ***ABS***: economically the most important group of anionic detergents (surface-active substances); a mixture of (R^1,R^2)-CH-C_6H_4-SO_3Na, where R^1 and R^2 = C_9 to C_{12}. They are made by sulfonation of alkylbenzenes with sulfur trioxide, followed by neutralization of the alkylbenzene sulfonic acids, usually with sodium hydroxide. A. are used mainly in powdered laundry products and liquid household cleansers.

Linear A., abb. ***LABS*** or ***LAS***, are biodegradable, in contrast to the highly branched, biologically "hard" ***tetrapropylenebenzene sulfonates*** used prior to the mid-1960's.

Alkyl halides: same as Haloalkanes (see).

Alkylidene-: a term for the atomic group R-CH= in a molecule, where R can be H or an alkyl group.

Alkylidine-: a term for the atomic group R-C≡C- in a molecule; with R = H (*ethylidine*), R = CH_3 (*propylidine*), etc.

Alkyl malonate esters: see Malonic ester syntheses.

Alkyl nitrates: R-O-NO_2, esters of alcohols and nitric acid. A. are pleasant-smelling liquids which explode when heated above their boiling points. They are obtained by reaction of alcohols with concentrated nitric or nitrating acid. Some important examples are Ethyl nitrate (see) and Glycerol trinitrate (see).

Alkyl nitrites: R-O-NO, esters of alcohols and nitrous acid. A. are made by reaction of dinitrogen trioxide with alcohols, or by reaction of alcohols with sodium nitrite as an equivalent amount of hydrochloric or sulfuric acid is added dropwise. A. are pleasant smelling liquids which are readily cleaved. Therefore, they are used instead of alkali nitrites in organic solvents to release nitrous acid (e.g. for diazotizations). The most important A. are Ethyl nitrite (see) and Isoamyl nitrite (see). A. with longer alkyl chains rearrange by a photochemical reaction into γ-nitrosoalcohols.

Alkyl sulfates: mono- and diesters of sulfuric acid.

1) ***Monoalkyl hydrogensulfates*** are most often used as the sodium salts, R-O-SO_3Na. These are white powders, readily soluble in water. A. of longer-chain alcohols, with 10 to 18 carbon atoms, are used as detergents, wetting agents and emulsifiers. Even small amounts of A. significantly reduce the surface tension of water and other solvents. They have the advantage over soaps that they form soluble compounds with Ca^{2+} and Mg^{2+} ions, and are not hydrolysed (neutral reaction). A. of primary alcohols (fatty alcohols) are made by sulfation with concentrated sulfuric acid, chlorosulfonic acid, sulfur trioxide, sulfur trioxide/pyridine or amidosulfonic acid. Secondary alcohols are sulfated with sulfuric acid and then neutralized. The surfactant properties of secondary A. are not as good as those of the primary A.

2) ***Dialkyl sulfates***, R-O-SO_2-O-R, are the neutral esters of sulfuric acid with alcohols. They are made by reaction of fuming sulfuric acid with alcohols in excess. A. are used as alkylating agents.

Alkynes: in the narrower sense, unsaturated hydrocarbons containing one C-C triple bond, with the general formula C_nH_{2n-2}. In the wider sense this class also includes hydrocarbons with several triple bonds, which can be isolated or conjugated; they are found widely in plants, e.g. in the Compositae. The A. form a homologous series of compounds (table) beginning with ethyne (acetylene).

Homologous series of alkynes

Ethyne (acetylene)	HC≡CH
Propyne	HC≡C−CH_3
But-1-yne	HC≡CH−CH_2−CH_3
But-2-yne	CH_3−C≡C−CH_3
Pent-1-yne	HC≡C−CH_2−CH_2−CH_3
Pent-2-yne	CH_3−C≡C−CH_2−CH_3
Hex-1-yne	HC≡C−CH_2−CH_2−CH_2−CH_3

Starting with butyne, structural isomerism with different positions for the triple bond become possible (but-1-yne and but-2-yne). However, since the triple bond is made up of sp-hybridized C atoms, there is no *cis-trans* isomerism.

For the nomenclature of A., see Nomenclature, sect. CIII.

Properties. Alk-1-ynes have higher boiling points than the corresponding alkanes. Ethyne, propyne and but-1-yne are gaseous at room temperature, and the higher homologs are liquid. The relatively higher boiling points are due to intramolecular attraction;

the A. have permanent dipole moments D, which in the alk-1-ynes range from 0.75 to 0.9. Compared to ethane and ethene, ethyne is more soluble in water and easier to liquefy, but liquid ethyne explodes violently when jarred or heated. Another property of ethyne and alk-1-ynes is that they are CH-acidic, i.e. that the H-atoms bound to the sp-hybridized C-atoms can be substituted by metal ions. The resulting metal compounds are called *acetylides*.

Reactions. *Addition reactions* are as typical of A. as of compounds with C-C double bonds (alkenes). Usually these reactions can be conducted in such a way that either substituted alkenes or the fully saturated alkane derivatives are formed. Triple bonds are more rapidly hydrogenated than double bonds, but in many other addition reactions, the reactivity of the A. is less than that of the alkenes. For further reactions, see Acetylene chemistry.

Analytical. The formation of copper(I) and silver(I) acetylides in ammoniacal solution can be used to detect A. with terminal triple bonds. In contrast to the alkenes, they do not react with tetranitromethane. The C≡C valence vibration appears in the IR spectrum in the range 2080 to 2280 cm^{-1}. The UV absorption of non-conjugated C≡C bonds occurs below 200 nm. In ^1H NMR spectra, the signals of acetylenic protons appear between δ 2 and 3 ppm. There are often long-range couplings, that is, couplings over more than three bonds.

Production. Only the most important A., ethyne (see Ethyne, sect. production), is produced industrially. Homologous A. or cycloalkynes can be synthesized by the following methods: 1) dehydrohalogenation of 1,2- or 1,1-dihalogen compounds or halogen vinyl compounds with alcoholic potassium hydroxide solution or sodium amide:

$$R\text{–}CHCl\text{–}CHCl\text{–}R \xrightarrow{KOH} R\text{–}CHCl\text{=}CH\text{–}R$$

$$\xrightarrow{KOH} R\text{–}C\equiv C\text{–}R \text{ or}$$

$$R\text{–}C(Cl)_2\text{–}CH_2\text{–}R \xrightarrow{KOH} R\text{–}C\equiv C\text{–}R.$$

2) Oxidation of bihydrazones of 1,2-diketones with mercury(II) oxide:

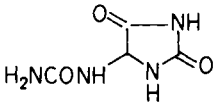
$$R\text{–}C(=N\text{–}NH_2)\text{–}C(=N\text{–}NH_2)\text{–}R \xrightarrow[-2H_2O/-2N_2]{+\,2O(HgO)} R\text{–}C\equiv C\text{–}R$$

Low-molecular-mass cycloalkynes like cyclopentyne or cyclohexyne can be formed in this way, although to date these highly strained compounds have only been demonstrated through subsequent reactions.

3) A. with terminal C-C triple bonds can be coupled to form alkadiynes by heating with copper(II) salts in pyridine (see Glaser reaction).

The applications of A. are based on their industrial availability and the many possible reactions (see Ethyne, Acetylene chemistry). Homologous A. are used for syntheses in scientific laboratories.

Allantoin, ***5-ureidohydantoin***: a degradation product of purine. It forms colorless crystals, m.p. 238.4 °C. A. is slightly soluble in water and alcohol, but dissolves readily in alkalies by forming salts. It is synthesized by oxidation of uric acid in a slightly alkaline medium, or by heating urea with dichloroacetic acid.



A. is found in the urine of many mammals (not including human beings and apes). It is formed from uric acid in the organism by the action of the enzyme uricase. The degradation of A. to ***allantoic acid*** is catalysed by the enzyme allantoinase. A. is also found in plants. It is used as an additive to cosmetics.

Allelochemicals: see Semiochemicals.

Allenes: unsaturated aliphatic hydrocarbons with two cumulative double bonds (see Dienes); the group is named for its simplest representative, ***allene (propadiene)***, $CH_2=C=CH_2$. Allene is a colorless, combustible gas; m.p. - 136 °C, b.p. - 34.5 °C, n_D^{20} 1.4168.

Typical reactions of the A. are base-catalysed isomerizations to alkynes and addition reactions similar to those of the alkenes. For example,

$$CH_2=C=CH_2 \xrightarrow{OH^-} HC\equiv C\text{–}CH_3$$

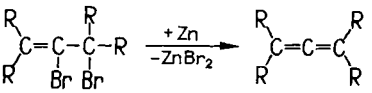
converts allene to propyne, while

$$CH_2=C=CH_2 + H_2O \xrightarrow{H+} CH_2=C(OH)\text{–}CH_3$$

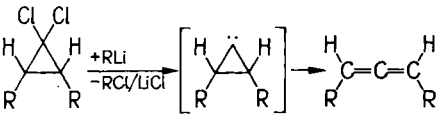
$$\rightarrow CH_3\text{–}CO\text{–}CH_3$$

converts allene to acetone. Homologous A. and large carbon rings with cumulative double bonds react in the same way, so that it is possible to synthesize cycloalkynes and cycloketones of the same ring size. Of the many methods of synthesis, the following are important:

1) Dehalogenation, e.g. debromination, of 2,3-dihaloalk-1-enes with zinc:



2) Cyclopropylidene-allene rearrangement. Lithium alkylene reacts with 1,1-dichlorocyclopropane, causing the three-membered ring to open; the reaction probably has a carbene intermediate:

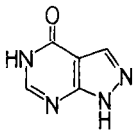


Since such cyclopropane derivatives are readily synthesized by dichlorocarbene addition to alkenes, this method is broadly applicable for synthesis of A.

Allethrin: see Pyrethroids.

Allomones: see Semiochemicals.

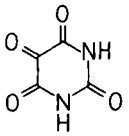
Allopurinol: a synthetic isomer of hypoxanthine which inhibits xanthine oxidase, the enzyme responsible for oxidative degradation of the purine skeleton to uric acid. In the presence of A., the danger of forming and depositing uric acid crystals (urate crystals) is reduced, because the purines are excreted as hypoxanthene, xanthine and uric acid. A. is used as a drug against gout.



Allose: see Monosaccharides, fig.

Allotropism: see Polymorphism.

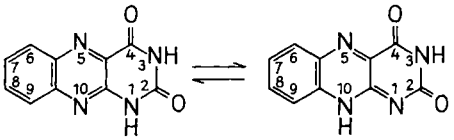
Alloxan, ***hexahydropyrimidine-2,4,5,6-tetrone***: the ureide of mesooxalic acid. A. forms yellow crystals which are readily soluble in water but insoluble in ether; m.p. 256°C (dec.). Solutions of A. give the skin a purple-red color. A. forms a colorless hydrate, ***alloxan hydrate***. It damages the pancreas, and is therefore used in animal experiments to induce diabetes. A. is a degradation product of uric acid.



It is synthesized by oxidation of barbituric acid with chromium(V) oxide, or of uric acid with nitric acid or potassium perchlorate in hydrochloric acid solution. A. is used in organic syntheses, and in the cosmetic industry to make lipsticks and self-browning skin creams.

Alloxan 5-oxime: same as Violuric acid (see).

Alloxazine, ***2,4-dihydroxybenzopteridine***: a heterocyclic ring system which is a tautomer of ***isoalloxazine*** (flavin). The isoalloxazine structure as such can exist only if the central nitrogen in position 10 has a carbon-containing substituent instead of hydrogen. A. is a gray-green powder, and its disodium salt forms yellow crystals. It decomposes above 300°C without melting; it is a weak acid. It is slightly soluble in alcohol, insoluble in water and ether, and readily soluble in alkali hydroxide solutions. It is made by condensation of o-phenylenediamine with alloxan. When heated with sodium hydroxide, it splits into urea and 2-hydroxyquinoline 3-carboxylic acid.



Alloxazine Isoalloxazine

Alloy: a metallic substance consisting of at least two metallic elements, or of one metallic and one nonmetallic element. The physical and chemical properties of the A. depend on the purity, isotropism and lattice defects in the crystals. The elements which make up an A. are called components; depending on the number of components, an alloy is called a *binary, ternary,* or *quaternary* A. A distinction is made between the base metal, which is the major component of the A., and the additives. The A. is named for the base metal (e.g. Aluminum alloys (see) or Copper alloys (see)), although the additives are often named as well to characterize the A. more fully (e.g. Iron-carbon alloys (see)). Nearly all the metals used in industry are A.

There are three limiting cases of A. structure: 1) phases with the character of compounds (see Intermetallic compounds), 2) solid solutions with complete or limited miscibility of the components (substitution and inclusion mixed crystals; see Mixed crystals), and 3) mixtures of pure components.

An A. is *homogeneous (monophasic)* if the crystallites all have the same structure and composition, even if they differ in shape, size or spatial orientation. An A. is *heterogeneous* if it consists of at least two different phases, e.g. two mixed crystal types with different concentrations, or a mixture of pure components (see Eutectic mixture). If the A. is at or near thermodynamic equilibrium, the solubility relationships of its phases can be expressed as functions of the temperature and pressure in a diagram of state. All A., with the exception of congruently melting intermetallic phases or eutectic mixtures, have a freezing or melting interval.

If thermodynamic equilibrium is not demanded, but only sufficient stability for use (metastable structures), there are further possibilities for production of A. Some examples of A. with nonequilibrium structures are the amorphous metals, also called metallic glasses, and highly disperse heterogeneous structures which consist of supersaturated mixed crystals.

The physical and chemical properties of the base metal are changed by alloying; for example, its mechanical strength and resistance to corrosion can be increased, but its electrical and thermal conductivity reduced. Often even very small concentrations of alloying elements are sufficient to cause a large change in properties (e.g. microalloyed steel).

A. are usually produced by melting the components together. To accelerate the process, the elements can be combined in a ***prealloy***, which contains the element in a higher concentration. High-melting components, or those which are immiscible in the liquid state, can also be alloyed by mixing and pressing their powders together, after which they are heated and pressed (sintered) into compact objects. A sintered material made by mixing powdered components which are not miscible in the liquid state is called a ***pseudoalloy***.

The classical method of producing pieces of A. is casting of blocks, heat working the blocks by hammering or rolling, and casting the metal into a mold (***casting A.***) or stamping it (***stamping A.***). Very pure pieces which are isotropic and free of macroscopic structural defects are made by special processes, such as the production of granulates by high-speed cooling and sintering the granulate by isostatic hot presses; electric slag remelting and casting, and thermomechanical working to increase the strength of the

A. structure. Reactive, high-melting metals are remelted by means of electric arcs, electron beams or plasma beams in high vacuum.

Mixtures of polymers, that is multicomponent systems consisting of organic polymers, are sometimes called ***polymer alloys***.

All-purpose cleanser: see Household cleansers.

Alphabet acids: sulfonic acids of the naphthalene series; their trivial names are constructed from a letter and the word "acid" (Table). Some of these compounds which are important in the production of azo dyes are also named for the authors who discovered them. Different colors of azo dyes can be obtained by choosing appropriate sulfonic acids for use as coupling components.

Some important alphabet acids

Trivial name	Systematic name
Tobias acid	2-Aminonaphthalene-1-sulfonic acid
Naphthionic acid	4-Aminonaphthalene-1-sulfonic acid
Peri acid	8-Aminonaphthalene-1-sulfonic acid
Nevile-Winther-acid	4-Hydroxynaphthalene-1-sulfonic acid
L acid	5-Hydroxynaphthalene-1-sulfonic acid
Cleve acid	4-Aminonaphthalene-2-sulfonic acid
1,6-Cleve acid	5-Aminonaphthalene-2-sulfonic acid
Schäffer acid	6-Hydroxynaphthalene-2-sulfonic acid
F acid	7-Hydroxynaphthalene-2-sulfonic acid
I acid	7-Amino-4-hydroxynaphthalene-2-sulfonic acid
G acid	7-Hydroxynaphthalene-1,3-disulfonic acid
R acid	3-Hydroxynaphthalene-2,7-disulfonic acid
H acid	4-Amino-5-hydroxynaphthalene-2,7-sulfonic acid

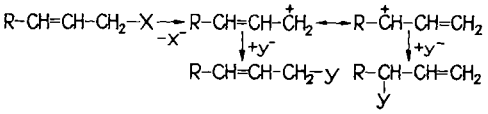
Allyl bromide, ***3-bromopropene***: $Br\text{-}CH_2\text{-}CH{=}CH_2$, a colorless, strongly lacrimatory liquid with an unpleasant odor; m.p. 119.4 °C, b.p. 71 °C, n_D^{20} 1.4697. A. is slightly soluble in water but dissolves readily in alcohol and ether. Its reactions are similar to those of Allyl chloride (see); it can be synthesized from allyl alcohol and hydrogen bromide or by bromination of propene at 300 °C. A. is used for organic syntheses.

Allyl chloride, ***3-chloropropene***: $Cl\text{-}CH_2\text{-}CH{=}CH_2$, a colorless liquid with a pungent smell; m.p. - 134.5 °C, b.p. 45 °C, n_D^{20} 1.4157. A. is slightly soluble in water, and readily soluble in most organic solvents. Under normal conditions, it is rather stable. As a bifunctional compound, it undergoes both the reactions typical of a C=C double bond and the usual halogen substitution reactions (see Haloalkanes). Allyl alcohol, allyl isothiocyanate and allylamine can be obtained from A. by nucleophilic exchange of the chlorine. A. is synthesized by chlorination of propene at 500 °C. It is used mainly in the production of glycerol, and is also used for the synthesis of other industrially important allyl compounds.

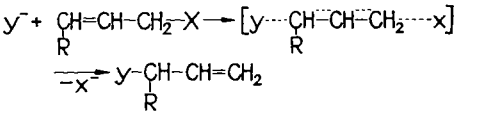
Allyl isothiocyanate: $CH_2{=}CH\text{-}CH_2\text{-}N{=}C{=}S$, a colorless, lacrimatory liquid with an odor similar to mustard; m.p. - 80 °C, b.p. 152 °C, n_{20}^D 1.5306. A. is a strong respiratory poison; it produces blisters and oozing, poorly healing ulcers on the skin. It is slightly soluble in water, and readily soluble in alcohol, ether and benzene. When stored for long periods under normal conditions, it decomposes. A. is present in the seeds of black mustard and horseradish roots, in the form of the glycoside sinigrin. When the glucoside is cleaved by the enzyme myrosin, A., glucose and potassium hydrogensulfate can be isolated. A. can be synthesized from allyl halides and silver rhodanide, or by isomerization of allyl rhodanide; this compound can be made from allyl halides and alkali rhodanides. A. is used as a perfume, germination inhibitor and insecticide.

Allyl substitution: radical substitution of a hydrogen atom in an alkene or cycloalkene in the allyl position by another atom or group. With chlorine, A. produces allyl chlorides at high reaction temperatures. Allyl bromides are formed by reaction with *N*-bromosuccinimide in carbon tetrachloride solution; the reaction is initiated with peroxides or UV light (see Wohl-Ziegler reaction). In certain alkenes, in which a stabilized cation intermediate can form, A. occurs by an addition-elimination mechanism.

Allyl rearrangement: a rearrangement of the allyl system observed in nucleophilic substitution reactions (see Substitution, 1) of allyl compounds. An intermediate allyl cation is formed by an S_N1 reaction. Because of the partial positive charges on the terminal C atoms of the allyl system, the nucleophilic reagent can react with either of these two atoms. The reaction product is formed by the S_N1' mechanism as a mixture of two structural isomers:



Certain steric conditions on the substrate and highly nucleophilic reagents can make the allyl substitution occur by an S_N2 mechanism with A.:



The reaction then takes place as a vinyl or normal S_N2 substitution, and leads to the rearrangement product (S_N2' mechanism) and/or the normal substitution product.

Aloe emodin: see Anthraglycosides.

Aloin: see Anthraglycosides.

Aloxidation: see Anodic oxidation.

Alpaka®: see New silver.

Alternating solid-liquid phase peptide synthesis: a method for synthesis of peptides using insoluble solid and soluble carriers. The principle of the A. is that a polypeptide chain is changed in the course of the coupling reaction so that the starting material and product are easily separated. The amino acid to be coupled is linked via its amino group to an insoluble polymeric carrier by an anchor group which can be selectively cleaved; the amino component is coupled to a soluble carrier. In the course of the reaction, the polypeptide is transferred to the solid phase. The product is separated by filtration and washing; after cleavage of the amino-protective group, the peptide re-enters the liquid phase and, depending on the carboxyl protective group and the chain length of the

peptide, it can be separated from excess polymer-linked amino acid by shaking, ultrafiltration, gel permeation chromatography or precipitation. The next synthetic cycle then begins with addition of the next N^{α}-polymer-bound amino acid. Although A. is flexible and has some methodological advantages, it has not yet been widely tested in practice. The method was used for synthesis of somatostatin on a scale of 100-500 g.

Alternative prohibition: a selection rule in vibration spectroscopy which says that for a molecule with a center of symmetry, a vibration can be active either in IR or in Raman spectroscopy, but not in both. See Infrared spectroscopy; Raman spectroscopy.

Altrose: see Monosaccharides, Fig.

Alum: a double salt of the type $M^{I}M^{III}(SO_4)_2 \cdot 12H_2O$, in which M^{I} = Na, K, Rb, Cs, NH_4 or Tl and M^{III} = Al, Ga, In, Sc, V, Cr, Mn, Fe or Co. The name A. is derived from that of the best-known representative of the group, potash alum (Potassium aluminum sulfate, see). The A. usually crystalize in well-formed octahedra or cubes. In the crystal lattice, both the monovalent and the trivalent metal ions are solvated by six water molecules each, yielding the dodecahydrate formula.

Aluminates: salts in which aluminum is part of the anion. ***Hydroxoaluminates***, with the composition $M^{I}[Al(OH)_4]$, $M^{I}_2[Al(OH)_5]$ or $M^{I}_3[Al(OH)_6]$, are obtained by dissolving aluminum hydroxide or aluminum in the corresponding metal hydroxide solutions. For example, $Al(OH)_3 + KOH \rightarrow K[Al(OH)_4]$. The tetrahydroxoaluminate ion can condense, via the dialuminate ion $[(OH)_3Al\text{-}O\text{-}Al(OH)_3]^{2-}$, to linear polymers; in this it resembles silicic acid. The polymers can be dehydrated at high temperatures to anhydrous A. with the composition $M^{I}AlO_2$, a compound based on cross-linked tetrahedral AlO_2^- units. These anhydrous A. can also be obtained by fusion of metal oxides with aluminum oxides, for example, $Na_2O + Al_2O_3 \rightarrow 2\ NaAlO_2$. The corresponding derivatives of many divalent metals are found in nature as spinels, e.g. $MgAl_2O_4$ or $ZnAl_2O_4$.

Aluminizing: a process by which an aluminum protective layer is added to steel or cast iron; the layer is highly resistant to scale formation, especially in the presence of hot combustion gases. By long diffusion of aluminum into the iron at high temperature, a zone of iron-aluminum mixed crystals is formed in the iron material; above it there are brittle intermetallic layers (Al_3Fe, Al_2Fe). The outer zone of the layer is nearly pure aluminum with residues of Al_3Fe and Al_2Fe. In ***calorization***, the object is heated in an aluminum or iron-aluminum alloy powder to which ammonium chloride and clay powder have been added. At a temperature of 850 to 1050 °C, the aluminum diffuses into the surface of the iron object. In ***dip aluminizing***, the object is dipped into an aluminum melt at 700 to 800 °C. In ***spray aluminization*** or ***alumetization***, melted aluminum is sprayed onto the surface of the object (see Metal spraying). In this case, the alloy layer is formed when the object is heated to higher temperature (about 800 °C). A. can be used to protect automobile mufflers, palettes for annealing of metal parts, parts for electric heating devices and metal stovepipes.

Aluminothermal process, *thermite process, Goldschmidt process*: a method introduced in 1894 for carbon-free production of metals which are difficult to reduce and melt at high temperatures (chromium, manganese, vanadium, cobalt, boron, silicon, iron, etc.). The metals are produced from their oxides by reduction with aluminum, e.g. $Cr_2O_3 + 2\ Al \rightarrow 2\ Cr + Al_2O_3$. The metal oxide is mixed with coarse aluminum powder, and ignited, usually with an ignition pellet of magnesium powder mixed with barium peroxide or potassium chlorate. The reaction is highly exothermic, and temperatures over 2000 °C are reached. The metal can therefore flow into a compact mass on which the slag floats. The reaction is driven by the high free energy of formation of aluminum oxide; this is a result of the high lattice energy of the oxide. The A. can also be used to weld iron parts, such as streetcar tracks by igniting a mixture of iron oxide and aluminum: $3\ Fe_3O_4 + 8\ Al \rightarrow 4\ Al_2O_3 + 9\ Fe$, $\Delta H = -2980\ kJ\ mol^{-1}$.

The Al_2O_3 slag which is always formed is synthetic corundum, and can be used as an abrasive and for fire-resistant coatings.

Aluminum, symbol ***Al***: an element of Group IIIa of the periodic system, the Boron-aluminum group (see). Al is a light metal and an isotopically pure element, Z 13, with atomic mass 26.98154, valence III, very rarely I, density 2.702, m.p. 660.37 °C, b.p. 2467 °C, electrical conductivity 40 Sm mm^{-1} (at 0 °C), standard electrode potential (Al/Al^{3+}) - 1.706 V.

Properties. Al is a silvery white, relatively soft, ductile metal crystallizing in a cubic face-centered lattice. It is easily rolled into thin foils or drawn into wire. Its tensile strength is 70 to 120 MPa, depending on the degree of purity. A. is an excellent heat conductor, and its electrical conductivity is about 65% of that of copper. At 600 °C, it takes on a granular structure. Stirring of a supercooled melt produces coarse aluminum powder, and fine powder is produced by pounding.

Al tends to give up its three valence electrons to form colorless Al^{3+} cations. Because of their high positive charge, these are highly hydrated in water. Solid aluminum salts also often contain $[Al(H_2O)_6]^{3+}$ cations. The strong reductive activity which might be expected from the high standard electrode potential is often not seen, because a solid, firmly attached layer of oxide forms on the surface of the metal (passivation). This oxide layer can be thickened by treating the Al with an oxidizing agent, or by electrolysis (eloxal process), which significantly increases its resistance to corrosion. Al treated in this way is stable to atmospheric components, water, dilute acids and bases. It also resists concentrated nitric acid, because of the oxide layer. If the layer is destroyed, for example by amalgamation, the Al reacts rapidly with air to form aluminum oxide, or with water to form aluminum hydroxide and hydrogen. Al dissolves in strong acids or bases with evolution of hydrogen: $Al + 3\ H_3O^+ \rightarrow Al^{3+} + 3/2\ H_2 + 3\ H_2O$; $Al + OH^- + 3\ H_2O \rightarrow [Al(OH)_4]^- + 3/2\ H_2$. Finely divided Al burns to give aluminum oxide, and releases heat: $4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$. The strong tendency of Al to oxidize is utilized in industry; for example, oxides dissolved in molten iron are removed by reduction with Al (deoxidation). Al is also used to prepare

many metals from their oxides (see Aluminothermal process). Al combines with halogens in exothermic reactions to form the aluminum halides (AlF_3, $AlCl_3$, etc.). These compounds are interesting because of their structures, but also because of their Lewis acidity. Al reacts with sulfur and nitrogen at very high temperatures, forming aluminum sulfide, Al_2S_3 or aluminum nitride, AlN. Compounds of Al with oxidation number +1 are obtained by reduction of aluminum(III) compounds with Al. They are endothermic compounds (e.g. Al_2O, AlF), and are stable only at high temperatures.

Analytical. The qualitative identification of Al in the ammonium sulfide group is made by precipitation as aluminum oxide hydrate, or as a color lake with alizarin S. Another qualitative test is the formation of $CoAl_2O_4$ (Thénard's blue) by heating aluminum hydroxide, $Al(OH)_3$, in the presence of cobalt(II) nitrate, $Co(NO_3)_2$. Al can be determined quantitatively by precipitation of the oxide hydrate, conversion of the precipitate to aluminum oxide by heating to red heat, cooling and weighing. Complexometric determination with EDTA is less cumbersome; this is usually done as a back titration. Very small concentrations of aluminum are detected by photometric techniques with various complex formers, such as Chromazurol S.

Occurrence. A. makes up 8.1% of the earth's crust, and is thus the third most abundant element, after oxygen and silicon, and the most abundant metal, before iron. It is always found in compounds in the form of various feldspars, glimmers, clays and bauxite. The most important Al minerals are orthoclase (potassium feldspar), $K(AlSi_3O_8)$, albite (sodium feldspar), $Na(AlSi_3O_8)$, anorthite (calcium feldspar), $Ca(Al_2Si_2O_8)$, muscovite, $KAl_2(AlSi_3O_{10})(OH,F)_2$, and cryolite, Na_3AlF_6. Clays of various compositions are formed by weathering of rocks containing feldspars. Clays containing silicon dioxide and iron oxide are called loams, while clays containing calcium or magnesium carbonate are called clay marls. Kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, is the starting material for mak-

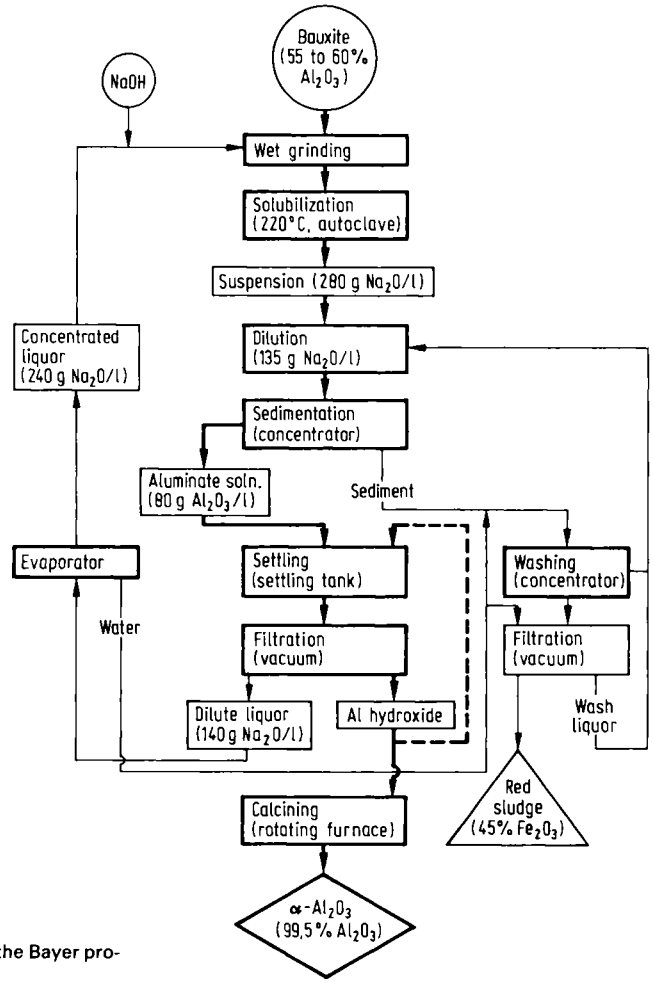


Fig. 1. Diagram of alumina production by the Bayer process.

ing porcelain. Pure aluminum oxide is found in the form of corundum; with chromium oxide impurities it is known as ruby, and when colored with titanium oxide, it is sapphire. Emery is also a form of aluminum oxide.

Al is a component of the soil and is also found in plant and animal tissues. However, it seems to be physiologically inert.

Al is extracted from oxidized ores. Aluminum oxide cannot be reduced carbothermically, because of the formation of Al_4C_3; however, Al-Si alloys can be produced in this way. Because of the high affinity of Al for oxygen, it is purified by electrolysis of a cryolite-alumina melt in which Al is the least reactive metal component. Reduction to the pure metal takes place in two steps: production of pure Al_2O_3 (aluminum oxide, alumina) and melt electrolysis of Al_2O_3 in molten cryolite (sodium fluoroaluminate), Na_3AlF_6.

1) Production of alumina. Nearly all alumina is produced from the sedimentary rock bauxite, which consists of aluminum and iron aquaoxides, calcium oxide and silicon dioxide. The Al_2O_3 content should be high (> 55%), and the SiO_2 content low (< 5%). Other minerals and sedimentary rocks with Al_2O_3 contents around 30% are now also used, e.g. alunite, $KAl_3[(OH)_6/(SO_4)_2]$ and nepheline, $KNa_3(AlSiO_4)_4$. It seems probable that clay deposits in which the main mineral is kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, will eventually become significant ores for alumina.

In most operations, pure aluminum is made by wet extraction of the ore by the *Bayer method* (Fig. 1). The Al compounds in the bauxite are dissolved in sodium hydroxide solution containing 200 to 350 g Na_2O/l at 160 to 240 °C and at a pressure of 0.8 MPa: $Al(OH)_3 + NaOH \rightleftharpoons Na^+ + [Al(OH)_4]^-$; the ratio of Na_2O:$Al(OH)_3$ is 1.7. Fe_2O_3 does not dissolve under these conditions, and SiO_2 is converted to insoluble sodium aluminosilicate (loss of NaOH and Al_2O_3). The alumina solution is cooled to 100 °C by decompression and diluted to 100 to 140 g Na_2O/l; the insoluble sludge is separated by filtration. The clear solution is further cooled to 60 °C, then hydrargillite seed crystals (γ-$Al(OH)_3$) are added. The crystallization occurs in 30 to 70 hours, in large, stirred vats. The $Al(OH)_3$ which crystallizes out is removed by filtration; 80% is used for seeding the extraction solution, and the remainder is dried in rotating or fluidized bed furnaces and calcined at 1200 to 1300 °C to obtain α-Al_2O_3. The filtered Na_2O solution is condensed and returned to the extraction process. The energetically expensive condensation process is avoided by use of extraction solutions containing only 140 g Na_2O/l, at higher temperatures.

Non-bauxite ores which are rich in SiO_2 (clays, alunite, nepheline, etc.) cannot be converted to pure Al_2O_3 by the Bayer process because of the formation of sodium hydroxyaluminosilicate, $3\ Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaOH$. The SiO_2 can be bound to CaO by basic extraction at high temperatures, or the aluminum can be extracted with mineral acids which do not dissolve the SiO_2.

In the basic *lime-sinter process*, nepheline or clay is thermally extracted with lime at 1300 °C in a rotating furnace; $(Na,K)AlO_2$ and Ca_2SiO_4 are formed. After leaching of the alkali metal aluminate from the porous sinter product with water or soda solution, the polymeric silicic acids are precipitated from the partially dissolved silicates in autoclaves at 150 to 175 °C and separated. CO_2 is then passed through the solution to precipitate the $Al(OH)_3$, which is calcined to alumina. Byproducts are alkali metal carbonates, obtained by evaporation of the mother liquor, and cement from the silicate residues.

Before it can be used for acidic extraction, kaolinite must be converted by thermal decomposition at 750 °C to acid-soluble metal kaolinite, $Al_2O_3 \cdot 2SiO_2$. The iron-containing impurities in the ore go into solution with the Al_2O_3. Although the recovery of the extraction acid and its corrosive effects on the equipment are problems, acid extraction will become more significant as time goes on, because of the shortage of bauxite. The advantages of the *sulfurous acid process* are the ready decomposition of aluminum sulfite and the circulation of SO_2; the crude aluminum hydroxide is worked up by the Bayer process. In the *sulfuric acid process*, pressurized extraction of clays does not dissolve the iron compounds; the subsequent pressure hydrolysis at 220 °C produces $H_3OAl_3(SO_4)_2(OH)_6$. In the *hydrochloric acid process*, the resulting $AlCl_3$ solution contains $FeCl_3$, which can be separated by liquid-liquid extraction. $AlCl_3 \cdot 6H_2O$ is crystallized out of the $AlCl_3$ solution and converted to alumina by thermal decomposition.

2) *Melt electrolysis*. Since melt electrolysis of pure Al_2O_3 would require a very high temperature, Al is produced from a melt of synthetic cryolite, Na_3AlF_6, in which 5% Al_2O_3 is dissolved. The electrolysis can then be done at 950 to 980 °C. The liquid cryolite dissolves the Al_2O_3 by forming a complex: $Al_2O_3 + [AlF_6]^{3-} \rightarrow 3\ [AlOF_2]^-$, and provides the current carriers (Na^+, $[AlF_6]^{3-}$, F^-). The fluoride is not consumed by the electrolysis, that is, the electrolytic decomposition produces Al at the cathode, and oxygen at the carbon anode, which reacts to form CO_2. The reaction mechanism is very complex and is still not completely elucidated; in simplified form the cathode and anode processes can be formulated as follows: $8\ AlF_3 + 12\ e \rightarrow 4\ Al + 4\ [AlF_6]^{3-}$; $2\ Al_2O_3 + 4\ [AlF_6]^{3-} + 3\ C - 12\ e \rightarrow 3\ CO_2 + 8\ AlF_3$.

Melt electrolysis is done in shallow carbon tubs. The anodes are suspended above the melt and dip into it; they consist of carbon blocks or self-combusting Söderberg electrodes (Fig. 2).

The practical decomposition voltage is 1.7 V; power consumption may be as high as 100 kW per cell. The production of 1 t Al requires 15 MWh of electricity, 1.9 t Al_2O_3 and 0.5 t carbon. The liquid Al collects on the bottom of the cell (cathode) and is sucked into a vacuum crucible. It is then either poured into ingots or remelted in large furnaces. Electrolysis Al is 99.9% pure Al.

Very pure Al, with a purity greater than 99.99%, is produced by three-layer electrolysis at 750 °C. The lowest layer is an alloy of 70% Al and 30% Cu, and serves as a liquid anode. It is covered by a layer of electrolyte melt, consisting of 60% $BaCl_2$, 24% AlF_3, 12% NaF and 4% NaCl. The top layer consists of liquid purified aluminum. The carbon cathodes are surrounded by the pure aluminum layer; they dip into the salt melt layer, where reduction to the metal occurs.

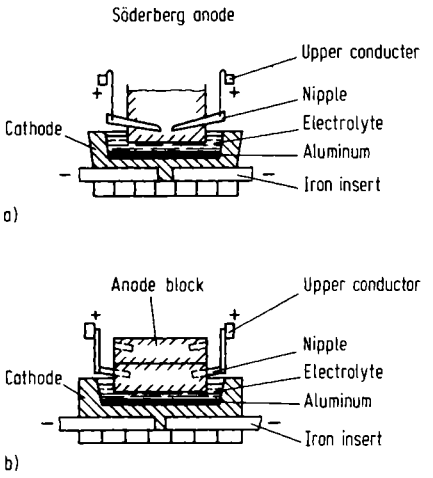


Fig. 2. Electrolysis cells for production of aluminum: *a* with Söderberg anodes; *b* with pre-fired continuous block anodes.

Recently, $AlCl_3$ melt electrolysis has been developed to the stage of industrial application. The electrolyte consists of 5% $AlCl_3$, 53% NaCl and 42% LiCl. The advantages are the low working temperature and thus the lower current consumption, and the advoidance of environmental contamination by release of fluorine-containing gases.

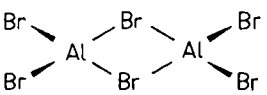
Applications. Its low density, favorable mechanical properties, good heat conductivity and ductility, and adequate resistance to corrosion make Al a valuable material for production of equipment, armatures, containers, etc. and for construction of vehicles and aircraft. Because of its high electrical conductivity, it is used in electrical cables and wires. Because it is not toxic, it is used to make tanks and containers for foods and beverages, cooking ware, aluminum foil, etc. Vacuum deposited layers of Al on glass make excellent reflective layers for light and heat; this is utilized, for example, in the construction of mirror telescopes. Aluminum powder is used to make rust-protective paints and for fireworks; coarse powder is used in metallurgy to produce various metals by the aluminothermal process. Al is also used as a filler and pigment. Most of the Al produced is alloyed (see Aluminum alloys).

Historical. The name A. is derived from the Latin "alumen" = "alum". This term appeared in the 5th century B.C. in the writings of Herodotus. Marggraf first produced alumina in 1754, and Oersted first produced the free metal in 1825 by reduction of the chloride with potassium amalgam. In 1827, Wöhler improved the process by reduction with potassium; he is considered the actual discoverer of Al. The first industrial process for Al production was developed by St. Claire Deville in 1854; he reduced $AlCl_3$ with the cheaper sodium. However, the high price prevented wide use of the new metal. Bunsen, Deville, Le Chatelier and others worked on methods for electrolytic production of Al, but the electrochemical process did not become practical before the invention of the dynamo by von Siemens in 1866/67. The year 1886 can be considered to have seen the birth of industrial Al electrolysis; in that year the Frenchman Heroult and the American Hall independently proposed electrolytic decomposition of aluminum oxide dissolved in cryolite. The process was developed in 1888 by Kiliani. The first hard Al alloy (duraluminum) was develped in 1906 by Wilm, and the three-layer process for very pure Al was introduced in 1919 by Hoopes.

Aluminum acetates: the aluminum salts of acetic acid. ***Aluminum triacetate***, $Al(OOCCH_3)_3$, is a neutral salt, while ***aluminum diacetate***, $HOAl(OOCCH_3)_2$, and ***aluminum monoacetate***, $(HO)_2AlOOCCH_3$, are basic. The A. are colorless solids which have not been well characterized. The triacetate is obtained by dissolving aluminum sulfate in lead or barium acetate solution, or from the reaction of aluminum hydroxide, glacial acetic acid and acetic anhydride. In aqueous solution, it forms basic aluminum acetates by hydrolysis. The diacetate can also be produced directly by reaction of sodium aluminate with acetic acid. The A. are used as mordants in dyeing. The diacetate can be used in treating cuts because of its astringent and antiseptic effect; it is called *acetic alumina*. Modern preparations contain tartaric acid as a stabilizer.

Aluminum alloys: alloys of aluminum, most often with copper, magnesium, manganese, silicon and zinc, but also containing small concentrations of nickel, lead, chromium, titanium and antimony. Iron is generally undesirable. The A. are harder than very pure aluminum, but they have lower electrical conductivity, and they are also often less resistant to corrosion. A. may be produced by casting or kneading. Thermal treatment of many A. increases their strength. This is true for ***duralumin*** (2.5 to 5.5% Cu, 0.2 to 0.5% Mg, 0.5 to 1.2% Mn and 0.2 to 1.0% Si), which has a density of 2.75 to 2.87 and is therefore used mainly for construction of vehicles and aircraft. Other important A. are ***hydronalium*** (3 to 12% Mg, 0.2 to 0.8% Mn and 0.2 to 1.0% Si), which is very resistant to seawater, and ***Silumin®*** (up to 14% Si), which is used as a pressure-resistant alloy in the construction of motors and other apparatus.

Aluminum bromide:, $AlBr_3$, forms colorless rhombic crystals which fume in moist air; K_r 266.71, D. 2.64, m.p. 97.5 °C, b.p. 263.3 °C. A. is a molecular solid consisting of Al_2Br_6 molecules; it is soluble in benzene and many other organic solvents. Two Br ions act as bridge ligands, giving the Al atoms electron octets. A. reacts violently with water, hydrolysing the Al-Br bonds. The solution is therefore very acidic. A. crystallizes out of aqueous solutions as the hexahydrate $AlBr_3 \cdot 6H_2O$; below - 9 °C, $AlBr_3 \cdot 15H_2O$ is formed. A. is produced by passing bromine gas over a glowing mixture of aluminum oxide and carbon, or by the direct reaction of bromine and aluminum. It is used as catalyst in organic syntheses such as the Friedel-Crafts reactions, polymerizations and brominations.



Al_2Br_6 molecule

Aluminum bronze: copper-aluminum alloy containing no more than 9% aluminum. The homogeneous copper-aluminum mixed crystals have excellent resistance to heat, corrosion and scaling. Multi-component bronzes with iron and nickel in addition to aluminum are also produced. A. are used to make acid-resistant parts for the chemical and food industries, for hot-steam armatures, valve seats, sliding parts, tooth and spiral gears. Ships' screws are cast from an alloy of 9.5% aluminum, 5% nickel, 4% iron, 1.5% manganese and the rest copper.

Aluminum carbide: Al_4C_3, forms colorless, hexagonal crystals; M_r 143.96, density 2.36, dec. 1400 °C. As an ionic carbide, A. is decomposed by acids to aluminum salt solutions and methane: $Al_4C_3 + 12\ HCl \rightarrow 4\ Al^{3+} + 12\ Cl^- + 3\ CH_4$. A. can be produced from the elements in an electric furnace.

Aluminum chloride: $AlCl_3$, forms a colorless hexagonal crystalline powder but, because of impurities, it usually appears light yellow. The crystals fume strongly in moist air and are hygroscopic. A. is soluble in many organic solvents; its M_r is 133.34, density 2.44, m.p. 190 °C at a pressure of 0.253 MPa, subl.p. 182.7 °C. In the liquid and vapor phases, and in some solvents, A. is dimeric, $Cl_2AlCl_2AlCl_2$, with four-fold coordinated aluminum in a structure analogous to that of Aluminum bromide (see). In solid A., the aluminum is 6-fold coordinated by Cl^-. Its solvation in water is strongly exothermic, involving hydrolysis of the largely covalent A. into chloride ions and hexaaquaaluminum ions: $AlCl_3 + 6\ H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3\ Cl^-$. The conversion of these cations into the hydroxo compound is responsible for the very acidic reaction of A.: $[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(H_2O)_5OH]^{2+} + H_2O^+$. Hexaaquaaluminum ions are also present in the rhombic hexahydrate, $AlCl_3 \cdot 6H_2O$, which crystallizes out of aqueous solution. When heated, this does not lose water of crystallization, but eliminates HCl to become basic aluminum chloride and finally, aluminum oxide. Water-containing A. can also be produced by dissolving aluminum in hydrochloric acid. Anhydrous A. is prepared by passing chlorine over a mixture of aluminum oxide and carbon at 800 °C, according to the equation: $Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3\ CO$, or it can be made directly from the elements: $2\ Al + 3\ Cl_2 \rightarrow 2\ AlCl_3$. Anhydrous A. is a strong Lewis acid used as a catalyst in organic syntheses, e.g. in Friedel-Crafts alkylations and acylations, dehydrogenations and polymerizations, and as a condensing agent and a halogen carrier. The hexahydrate is used in the soap and textile industries, in deodorants, as an antiseptic, to protect wood, etc.

Aluminum fluoride: AlF_3, a colorless, triclinic crystalline powder which is barely soluble in water and organic solvents; M_r 83.98, density 2.88, subl.p. 1291 °C. Several hydrated forms are also known. A. is an industrially important compound produced by passing hydrogen fluoride over red-hot aluminum or aluminum oxide: $Al_2O_3 + 6\ HF \rightarrow 2\ AlF_3 + 3\ H_2O$. A. forms complex salts of the type $M^I_3[AlF_6]$ with metal fluorides, for example the reaction of sodium fluoride produces sodium hexafluoroaluminate, $Na_3[AlF_6]$. A. is used in metallurgy as a flux and is also used in aluminum production.

Aluminum hydride, ***alane***: $(AlH_3)_x$, a colorless powder which decomposes above 100 °C into hydrogen and aluminum. A. is extraordinarily sensitive to oxidation and moisture. It reacts vigorously with water to release hydrogen: $AlH_3 + 3\ H_2O \rightarrow Al(OH)_3 + 3\ H_2$. A. forms Alanates (see) with many metal hydrides. The simplest synthesis of A. is the reaction of aluminum chloride with lithium alanate: $AlCl_3 + 3\ LiAlH_4 \rightarrow LiCl + 4\ AlH_3$. The compound is formed as the etherate, $H_3Al\text{-}C(C_2H_5)_2$, which is a monomer; it gradually polymerizes to A.

Aluminum hydroxide: There are two forms, ***aluminum orthohydroxide***, $Al(OH)_3$, and ***aluminum metahydroxide (aluminum oxygen hydroxide)***, AlO(OH). Three modifications of $Al(OH)_3$ are known, monoclinic hydrargillite (α-$Al(OH)_3$), hexagonal bayerite (β-$Al(OH)_3$) and γ-$Al(OH)_3$. AlO(OH) has two modifications, the orthorhombic boehmite (α-AlO(OH)), and rhombic diaspore (β-AlO(OH)). If A. is precipitated by adding ammonia to an aqueous aluminum salt solution, the compound is obtained in a voluminous, amorphous form known as ***aluminum oxide hydrate***. This very slowly changes, via boehmite and bayerite, to the thermodynamically stable hydrargillite. If carbon dioxide is passed through a sodium aluminate solution at 80 °C, crystalline α-$Al(OH)_3$ forms directly. However, if the precipitation is done below room temperature, or if the high-temperature precipitation is done too quickly, the first product is bayerite, which slowly converts to α-$Al(OH)_3$. If hydrargillite is heated in an autoclave to 300 °C, it is partially dehydrated to crystalline boehmite. Diaspore is made by heating boehmite in aqueous sodium hydroxide to 280 °C, under 50 MPa pressure. All forms of A. are dehydrated to aluminum oxide, Al_2O_3, by strong heating.

A. is amphoteric; it dissolves in acids to give the corresponding aluminum salt solutions, and it is converted by bases to aluminates: $Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^-$. The reactivity depends on the form of the A.; for example, crystalline $Al(OH)_3$ dissolves very much more slowly in acids than the amorphous product. Hydrargillite and diaspore are components of natural bauxite. Bayerite and hydrargillite are important as intermediates in the production of aluminum.

Aluminum nitrate: $Al(NO_3)_3 \cdot 9H_2O$, colorless, hygroscopic, rhombic crystals, m.p. 73.5 °C, dec. 150 °C, M_r 375.13. A. is soluble in water, alcohol and acetone. It is made by dissolving aluminum hydroxide in nitric acid, and is used as a mordant in dyeing.

Aluminum nitride: AlN, blue-gray, hexagonal crystalline powder, M_r 40.99, density 3.26, m.p. in N_2 atmosphere, 2200 °C, subl. p. 2000 °C, Mohs hardness 9 to 10. Water very slowly and incompletely hydrolyses A. to aluminum hydroxide and ammonia; in sodium hydroxide solution, A. is decomposed to ammonia and aluminate solution: $AlN + NaOH + 3\ H_2O \rightarrow NH_3 + Na[Al(OH)_4]$. A. is made by heating aluminum oxide with carbon and nitrogen in an electric furnace: $Al_2O_3 + 3\ C + N_2 \rightarrow 2\ AlN + 3\ CO$.

Aluminum oxide, ***alumina***: Al_2O_3. The important modifications are the cubic γ-Al_2O_3 and the rhombic corundum (α-Al_2O_3). γ-Al_2O_3 is a colorless, loose, hygroscopic powder which does not dissolve in water, but does dissolve in strong acid or base. It is made by

cautious dehydration of hydrargillite or boehmite (see Aluminum hydroxide). Above 1000 °C, it is converted into α-Al_2O_3, which is not soluble in acids or bases; M_r 101.96, density 3.97, m.p. 2015 °C, b.p. 2980 ± 60 °C.

α-Al_2O_3 is made in large amounts as an intermediate in the production of aluminum metal, and also occurs in nature as corundum. It has a Mohs hardness of 9, and is therefore used as an abrasive, in bearings for watches and analytical instruments, etc. Sintered α-Al_2O_3 (sintered corundum) is fire-resistant and is used to make laboratory crucibles and furnace cladding. Cutting tools are also made from sintered corundum. Rubies and sapphires are forms of corundum containing small amounts of Cr_2O_3 and TiO_2, respectively, as impurities. These gemstones, which are now important in laser technology, are prepared by melting the corresponding mixed metal oxides in an oxyhydrogen flame. A. forms Aluminates (see) in stoichiometric proportions with various metal oxides.

γ-Al_2O_3 is a very porous material. Its surface structure depends strongly on the temperature at which it is produced, and it is used widely as an adsorbent. It is also used as a catalyst and a carrier for other catalysts.

Aluminum oxide hydrate: see Aluminum hydroxide.

Aluminum oxygen hydroxide: see Aluminum hydroxide.

Aluminum phosphate: ***Aluminum orthophosphate***, $AlPO_4$, is a colorless, rhombic crystal powder, M_r 121.95, density 2.566, m.p. 1500 °C. It is insoluble in water, but dissolves in acids and bases. It is formed by adding sodium phosphate to an aluminum salt solution. In nature it occurs in the form of double salts, as wavellite, $Al_3(PO_4)_2(F,OH)_3 \cdot 5H_2O$, and turquoise, $Al(OH)_3 \cdot AlPO_4 \cdot H_2O$. It is used in the ceramics industry to make glazes. ***Aluminum metaphosphate***, $Al(PO_3)_3$, is a colorless, tetragonal crystalline powder; formula mass 263.90, density 2.779. It is insoluble in water and acids; its structure is based on long-chain and cyclic polyphosphate ions. It is formed by reaction of aluminum hydroxide with excess orthophosphoric acid and heating the mixture above 300 °C. It is used to prepare glazes, enamels, etc.

Aluminum silicates: crystalline silicates in which the aluminum has the cation function, in contrast to the Alumosilicates (see). The aluminum cation is octahedrally coordinated by oxygen atoms. In many clays, the aluminum is bifunctional (aluminum alumosilicates).

Aluminum sulfate: $Al_2(SO_4)_3$, a colorless powder; M_r 342.15, density 2.71. A. dissolves in water, giving an acidic reaction, and crystalizes out of this solution at room temperature as monoclinic $Al_2(SO_4)_3 \cdot 18H_2O$. It also forms hydrates with 6, 10 and 27 moles water. At 340 °C, the salt is completely dehydrated, and above 770 °C, it decomposes to aluminum oxide, Al_2O_3, and sulfur trioxide, SO_3. The hydrate is obtained by dissolving pure aluminum oxide in concentrated sulfuric acid. A. forms double salts with sulfates of monovalent metals; these have the composition $M^IAl(SO_4)_2 \cdot 12H_2O$ (see Alum). A. is used in the paper industry as sizing; it is also used as a mordant in dyeing, as a protective coating for seeds, to treat water and as a component of antifoaming agents.

Alumon: see AMO explosive.

Alumosilicates: silicates in which some of the SiO_4 tetrahedra are replaced by isomorphic AlO_4 tetrahedra. The additional positive charge required to neutralize the AlO_4 is supplied by incorporation of an equivalent number of cations (usually alkali or alkaline earth metal cations). Potassium feldspar, $KAlSi_3O_6$, is a typical A.; in it, every fourth silicon atom in the anionic network structure is replaced by an aluminum atom. The amount of substitution is limited; according to a rule of Loewenstein, AlO_4 tetrahedra can be linked only to SiO_4 tetrahedra. Other examples of A. are zeolites, ultramarine and clay minerals.

Alytensin: see Bombesin.

Am: symbol for Americium.

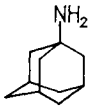
Amadori rearrangement: the rearrangement of glycosylamines (*N*-glycosides) into 1-amino-1-deoxy-2-ketoses. These compounds are made, for example, by reaction of aldoses with aromatic amines. The first products are glycosylamines, which rearrange on heating, in an acid- or base-catalysed step, into arylaminoketoses. A. corresponds to isomerization of the aldoses (see Monosaccharides).

Amalgamation: an enrichment step in the extraction of metals, expecially gold and silver, from their ores. The noble metal is dissolved in mercury, which has the capacity to form amalgams with many metals (see Mercury alloys). Gold or silver can be recovered from the amalgam by distilling off the mercury. A. can only be used with gold particles above a certain minimum size, because smaller particles are not sufficiently wetted by the mercury. A. has been largely replaced by Cyanide leaching (see).

Amanin: see Amatoxins.

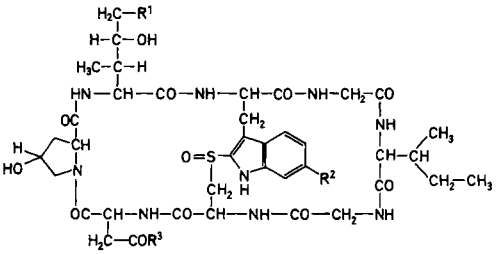
Amanitins: see Amatoxins.

Amantadine: 1-aminoadamantane, a cycloalkylamine which was developed as a virostatic for prevention of flu. Other cycloalkylamines and 1-aminoadamantane derivatives with substituents on the N atom also have antiviral effects. The main use of A. at present is in the therapy of Parkinson's disease.



Amaranth, ***Red no. 2***: a dark, reddish-brown powder, soluble in water and very slightly soluble in alcohol. It is made by diazotization of naphthionic acid and development with naphth-2-ol-3,6-disulfonic acid. It is used to dye wool and silk bright bluish-red from an acid bath, as an indicator in hydrazine titrations, and in color photography. It has been banned by the FDA for use in foods, drugs or cosmetics.
Formula, see Fast red (p. 400), where R, R_3 and R_6: $-SO_3Na$ and R_2: -OH.

Amatoxins: bridged, heterodetic, cyclic octapeptides which, together with the phallotoxins, are the most important toxins in the death cap mushroom *Amanita phalloides*. The A. include α-, β- and γ-amanitin and amanin (Fig.) and are found in high concentrations (0.2 to 0.4 mg/g fresh weight) in *Amanita phalloides*, *A. virosa* and in other mushrooms, including some in the genus *Galerina* and *Lepiota*. At a concentration of 10^{-8} M, A. inhibit the DNA-dependent RNA polymerase. By blocking protein biosynthesis at the level of transcription, they cause necrosis of a large fraction of the liver cells. Although the effects of A. probably begin within half an hour, the liver cells do not die until the second or third day after the poison has been consumed. Over 90% of the fatal mushroom poisonings are due to the A. The toxic effects of α-amanitin can be reversed, under special conditions, by antamanide, which is also found in the death cap fungus. The LD_{50} for the A. are about 0.5 mg/kg in the mouse. The structures and syntheses of the A. were reported by Th. Wieland et al.



Amatoxin	R^1	R^2	R^3
α-Amanitin	−OH	−OH	$-NH_2$
β-Amanitin	−OH	−OH	−OH
γ-Amanitin	−H	−OH	$-NH_2$
Amanin	−OH	−H	−OH

Ambazone: 1-amidinohydrazono-4-thiosemicarbazono-2,5-cyclohexadiene; a compound used as an oral disinfectant.

Amber, ***succinite***: a fossil resin which is a mixture of different compounds. Its average composition is 78% carbon, 10% hydrogen, 11% oxygen, 0.4% sulfur, etc. A. is transparent to translucent, and its color ranges from light yellow to orange and yellowish red, brown, yellowish white, sometimes striped, and also skyblue to dark blue. Buried A. is covered by a weathered layer which is often lacking from A. which has been recovered from water. A. is amorphous and has conchoidal breaks; it is brittle and has a Mohs hardness of 2 to almost 3. Its density is 1.050 to 1.096. A. burns with an aromatic odor (incense odor) and it is an excellent insulator for electric current. Rubbed A. acquires a negative charge. It melts around 375 °C, and it dissolves only partially in alcohol, ether, chloroform, terpentine oil, etc. When it is dry distilled, oil of amber and succinic acid are released as volatiles; the residue is A. colophony, which has a green fluorescence. A. is not dissolved by hydrofluoric acid or alkalies.

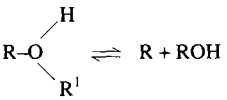
A. is the resin of Lower Tertiary pines and firs (mainly *Pinus succinifera*) which was washed into the sea in the early Oligocene and deposited together with clay, sand and gravel as "blue earth". Insects, spiders, feathers and parts of plants are often preserved in the resin, which was originally soft. It is thrown up along the entire coastline of the Baltic and North Seas.

A. is used mainly to make ornaments and objets d'art. Oil of A., a steam-distillable oil obtained by distillation of A. scraps, is used in paints.

Ambident ligand: see Coordination chemistry.

Ambidence: the presence of two or more centers (atoms) in a reagent where reactions can take place. Some examples of ***ambident*** or ***ambifunctional reagents*** are, the nucleophilic nitrite, cyanide, phenolate and enolate ions. Nucleophilic substitution reactions with these reagents often produce mixtures of products. Primary and secondary alkyl halides react with ambident nucleophiles by an S_N2 mechanism (see Substitution, 1), preferentially at the center of higher polarizability or lower electron density (center of greatest nucleophilicity). Tertiary alkyl halides, however, react by an S_N1 mechanism. The intermediate alkyl cation attacks the nucleophilic reagent on the atom with the highest electron density or lowest polarizability (see Kornblum rule).

A1 mechanism: the rate-determining step in S_N1 reactions (see Substitution 1.1). A protonated intermediate is cleaved in a monomolecular step:



Because they are highly nucleophilic, it is not possible for hydroxy or alkoxy groups to be split off as the anions OH^- or RO^- in substitution and elimination reactions.

A2 mechanism: bimolecular cleavage of a protonated intermediate involving a nucleophilic reagent. Especially in S_N2 reactions (see Substitution 1.2), the leaving tendency of the charged group of the oxonium ion may be too low to permit a monomolecular reaction step; however, the reaction does occur with the help of a nucleophile.

Ameletin: see Scotophobin.

Ameliotex: see Synthetic fibers.

Americium, symbol ***Am***: a radioactive element which is available only through nuclear reactions; it is a member of the actinide series in the periodic table (see Actinides). Am is a heavy metal, atomic number 95. The known isotopes have the following mass numbers (in parentheses the decay type, half-life and nuclear isomers): 232 (spontaneous decay; 1.4 min), 234 (spontaneous decay, 2.6 min), 237 (K-capture; α; 75 min; 2), 238 (K, α; 1.6 h; 2), 239 (K, α; 11.9 h; 2), 240 (K, α; 50.8 h; 2), 241 (α; 433 a; 2), 242 (β^-, K; 16.01 h; 3), 243 (α; 7400 a; 2) 244 (β^-, K; 26 min; 3) 245 (β^-; 2.05 h; 2); 246 (β^-; 25 min; 3), 247 (β^-; 22 min). The atomic mass of the most stable isotope is 243. The valence is III, sometimes also II, IV, V, VI, VII; density 13.671, m.p. 1173 °C, b.p. 2610 °C, standard electrode potential (Am/Am^{3+}) - 2.320 V.

Am is a silvery white, very soft metal which occurs in two modifications. Its chemistry is very similar to that of plutonium; it can be obtained in the metallic

state by reduction of americium (III) fluoride with barium at 1100 to 1200 °C or by reduction of americium(IV) oxide with lanthanum. During enrichment of Am, lanthanides are used as carrier substances; Am can be separated from them by fractional fluoride precipitation, because americium(III) fluoride is somewhat more soluble than the lanthanide fluorides.

Am was discovered in 1944 by the Americans Seaborg, James, Morgan and Ghiorso in the form of the isotope ^{241}Am; it was the product of neutron irradiation of plutonium 239 in a nuclear reactor:

$$^{239}_{94}Pu \xrightarrow[-\gamma]{+n} {}^{240}_{94}Pu \xrightarrow[-\gamma]{+n} {}^{241}_{94}Pu \xrightarrow[(14.89a)]{-\beta^-} {}^{241}_{95}Am$$

Americium 241 is now available on the 100-g scale. As a β-emitter, it is converted into the long-lived neptunium 241. The most stable americium isotope, ^{243}Am, is also obtained by neutron bombardment of plutonium 239; it is now available on the 10-g scale.

Am is determined radiometrically, spectrophotometrically or gravimetrically by precipitation as americium(III) hydroxide or oxalate, then calcination to the dioxide, AmO_2, above 450 °C.

Am was named as a parallel to the lanthanide with the comparable electron configuration, europium.

Americium compounds: compounds in which americium is most often in the +3 oxidation state, but is also frequently in the +2 state; in this respect it is similar to the homologous lanthanide, europium. Compounds in which americium is in the +4, +5, +6 or +7 state are similar to the corresponding plutonium compounds. Americium(II) compounds can be obtained from americium(III) compounds by reduction with sodium amalgam. ***Americium(II) sulfate***, $AmSO_4$, like $EuSO_4$, is barely soluble in water. When americium(III) nitrate or oxalate is heated in an oxygen atmosphere to 700 to 800 °C, ***americium(IV) oxide***, AmO_2, is formed. This is a black compound which crystallizes in a fluorite lattice; M_r 275.13, density 11.68. When it is heated with tetrachloromethane, at temperatures between 800 and 900 °C, ***americium(III) chloride***, $AmCl_3$ is formed; this forms pink, hexagonal crystals which sublime at 850 °C; M_r 349.49, density 5.78. ***Americium(III) bromide***, $AmBr_3$ (pink, orthorhombic crystals, M_r 482.86), and ***americium(III) iodide***, AmI_3 (yellow, orthorhombic crystals, M_r 623.84, density 6.9) can be made by reaction of AmO_2 with the corresponding aluminum halides. ***Americium(III) fluoride***, AmF_3 (light pink, hexagonal crystals, M_r 300.12, density 9.53), is obtained from the reaction of hydrofluoric acid with AmO_2 at 650 °C. Americium(III) halides are isotypes of the trihalides of plutonium and neptunium. ***Americium(III) oxide***, Am_2O_3 (red-orange cubic or hexagonal crystals, M_r 534.26), is formed by reduction of AmO_2 with hydrogen at 600 °C. High-temperature reactions of americium(III) compounds with fluorine lead to yellow-brown ***americium(IV) fluoride***, M_r 318.89. This compound is an isotype of other actinide(IV) fluorides AnF_4, where An = U, Np, Pu, Cm. AmF_4 reacts with alkali metal fluorides to form fluoro complexes of the type $[AmF_5]^-$, $[AmF_6]^{2-}$ and $[AmF_8]^{4-}$.

Strong oxidizing agents, such as peroxodisulfate, convert americium to the +5 and +6 oxidation states. The resulting linear cations, AmO_2^+ and AmO_2^{2+}, are yellow-brown and red-brown, respectively. Americium(V) and americium(VI) compounds tend to disproportionate. For example, in acidic solution, americium(V) is observed to disproportionate into americium(III) and americium(VI) according to the equation $3\ AmO_2^+ + 4\ H^+ \rightleftarrows Am^{3+} + 2\ AmO_2^{2+}$. In strongly alkaline solution, americium(VI) compounds disproportionate to americium(V) and the very unstable americium(VII) compounds: $2\ AmO_2(OH)_2 + 3\ OH^- \rightleftarrows AmO_2OH + AmO_5^{3-} + 3\ H_2O$.

The americium(VI) complex $Na[AmO_2(CH_3COO)_3]$ is obtained by oxidation of americium(III) with peroxodisulfate in acidic solution in the presence of sodium acetate.

Amiben: see Herbicides.

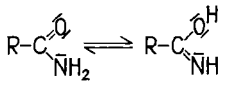
Amide: 1) a derivative of an inorganic (see Cyanamide) or organic acid in which an OH group is replaced by an amino group. The H atoms of the amino group can be replaced by other groups R^1 and R^2. Most A. have trivial names derived from the trivial names of the acyl group, in which the -yl ending is replaced by -amide, as in acetamide. The systematic name is based on that of the acid, with the ending "-ic acid" replaced by "-amide". With the exception of the liquid formamide, A. are crystalline solids at room temperature. They are hydrolysed by aqueous acids or bases, releasing the acid. A. are amphoteric, and form salts with strong acids and bases. They display Amide-iminol tautomerism (see) and can be reduced with strong reducing agents (Na/ethanol, $LiAlH_4$). Amines are also formed by catalytic hydrogenation of A. Hofmann degradation (see) or degradation with lead(IV) acetate produces the amine with one C atom fewer. Organic A. are synthesized by heating ammonium salts of the carboxylic acids, or the carboxylic acids themselves, with urea; by reaction of carboxylic acid anhydrides, halides or esters with ammonia or primary or secondary amines; by partial hydrolysis of nitriles, by Beckmann rearrangement (see), the Gattermann-Hopff reaction (see), the Willgerodt-Kindler reaction or by the reaction of arenes with isocyanates. When an A. is formed between the carboxyl group of an amino acid and the amino group of a second amino acid, the result is called a Peptide bond (see). Polyamides are made by reaction of di- or polycarboxylic acids with di- or polyamines. Thioamides are formed from thiocarboxylic acids, amidines from imidoesters and ammonia, and sulfonamides from sulfonic acids and amines. Reactions with aniline yield the corresponding anilides. Replacement of a hydrogen atom in the NH_3 molecule by a metal atom gives a metal amide (e.g. sodium amide). Formamide and *N,N*-dimethylformamide are common solvents; the latter is used as a formylating reagent in the Vilsmeier-Haack reaction (see). Urea is the diamide of carbonic acid.

2) A compound formed by substitution of a metal atom for an H atom in ammonia, with the general formula M^INH_2; an example is sodium amide.

Amide degradation: see Hoffmann degradation.

Amide hydrazone: see Amidrazone.

Amide-iminol tautomerism: a tautomeric equilibrium between an acid amide and a non-isolable iminol form:



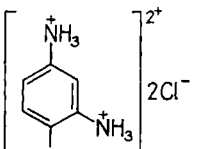
Amide form Iminol form

The equilibrium lies far on the amide side, but derivatives of the iminol form are known: imide halides and imidoesters. A special case of A. is Lactam-lactim tautomerism.

Amide resins, ***amino resins***, ***amino plastics***: polycondensation products made from amines and aldehydes, usually formaldehydes. The A. are classified according to the amine used as 1) protein-formaldehyde plastics, 2) aniline resins, 3) urea resins, 4) melamine resins and 5) dicyanodiamide resins. The production of protein-formaldehyde plastics, such as artificial horn, and of aniline resins has declined compared to other A. The urea and Melamine resins (see) are now the most important A., but the Dicyanodiamide resins (see), which were first developed in the 1960s, are growing in importance because they are more temperature-resistant than urea resins. A. are generally molded to make various articles; they are also used as molded sheets, glues and foams, textile additives, bonders for plastic parts and as paint bases.

Amidines: nitrogen-containing derivatives of carboxylic acids with the general formula R-C(=NH)-NH_2. The H atoms of the strongly basic amidine or guanyl group may be replaced by aliphatic, aromatic or heterocyclic groups. A. are readily hydrolysed in the presence of water, forming carboxylic acid amides and ammonia or amines. Their salts are much more stable. A. can be synthesized by the reaction of ammonia or amines and imino esters: R-C(=NH)-OR^1 + NH_3 → R-C(=NH)-NH_2 + R^1OH. Unsubstituted A. are important starting materials for production of nitrogen-containing heterocycles, e.g. imidazoles and pyrimidines, which are used in the manufacture of drugs.

Amidol, ***2,4-diaminophenyldihydrochloride***: colorless to gray crystals, sinters at 227 °C, m.p. 230-240 °C (dec.). A. is very soluble in water. It is synthesized by reduction of 2,4-dinitrophenol to 2,4-diaminophenol, a compound with leaflet crystals, m.p. 78-80 °C (dec.). A. is a high-quality, non-streaking photographic developer. It is also used to dye furs and hair.



Amidosulfonic acid, formerly ***sulfaminic acid***: H_2N-SO_3H, colorless, orthorhombic crystals, M_r 97.09, density 2.126, m.p. 200 °C (dec.). A. is soluble in water and gives an acidic reaction. It is synthesized by reaction of chlorosulfuric acid or sulfur trioxide and ammonia, or by reaction of urea with sulfuric acid or oleum. A. is used in the textile industry, in galvanizing, in pesticides and as a reagent to detect and destroy nitrites. Its acid properties are utilized in the removal of calcium deposits and as a component of bubbling bath salts, etc.

Amido trizoate: see X-ray contrast media.

Amido yellow E.: see Nitro dyes.

Amidrazone: a term for a nitrogen-containing carboxylic acid derivative with the general formula R-C(=N)-NH-NH_2 or R-C(=N-NH_2)-NH_2. Depending on the position of the double bond, these compounds are also called ***hydrazide imides*** or ***amide hydrazones***. A. are formed by reaction of hydrazine and imino esters: R-C(=NH)-OR^1 + H_2N-NH_2 → R-C(=NH)-NH-NH_2 + R^1OH.

Amikacin: see Kanamycins.

Aminals: organic compounds with the general formula R-CH(NR_2)$_2$. They are formed by the reaction of an aldehyde, in which there is no α-hydrogen atom, with a secondary amine; water is split off:

Amination: a reaction which introduces an amine group, -NH_2, -NHR or -NR_2, into a compound. A. is essentially a substitution reaction in which compounds with reactive halogen atoms are converted to the corresponding substituted amino derivative by reaction with ammonia or an amine (see Aminolysis). In some cases, hydroxy or sulfonic acid groups can be replaced by amino groups. Some other possibilities for A. are offered by the Čičibabin reaction for pyridines and the addition of primary and secondary amines to alkynes.

Amine: an organic compound in which, formally, one or more of the hydrogen atoms in ammonia is replaced by a carbon atom. The substituents can be aliphatic or aromatic hydrocarbons or heterocycles. Primary A. have one substituted hydrogen atom, R-NH_2, secondary A. have two, R_2NH, and tertiary A. have three, R_3N. The substituents on the nitrogen atom can be identical or different. There are also compounds with quaternary nitrogen atoms, the quaternary ammonium hydroxides (R_4N^+)OH^-, and their salts, (R_4N^+)X^-, and simple ammonium salts, which can have one, two or three substituents (e.g. (R_3HN^+)X^-).

The number of amino groups on a molecule is indicated by a prefix such as mono-, di-, tri-, etc., as in "diamine".

The name of an aliphatic monoamine is derived from the name of the hydrocarbon group to which the N atom is bound, followed by the suffix "-amine". Examples are methylamine, CH_3-NH_2, ethylamine, CH_3-CH_2-NH_2, dimethylamine, CH_3-NH-CH_3, trimethylamine, $(CH_3)_3N$, or benzylamine, C_6H_5-CH_2-NH_2. With primary aliphatic amines, it is also possible to construct the name from the root for the hydrocarbon and the prefix "amino-", as in aminoethane, CH_3-CH_2-NH_2. Similarly, di- and triamines and arylamines are considered amino-substituted hydrocarbons, for example, 1,3-diaminopropane, NH_2-$(CH_2)_3$-NH_2, or aminobenzene. There are also a number of trivial names which are either permitted by IUPAC or are in common use, e.g. aniline, ethylenediamine, putrescine and cadaverine.

Properties. The first two members of the homologous series, methyl- and ethylamine are gaseous, combustible compounds with an ammonia-like odor. The next aliphatic A. are liquids with fishy odors, while those with larger molecules are solids and have

no odors. Arylamines are liquid or solid, have unpleasant odors, and slowly turn brown in the air, due to oxidation. The aromatic A. are highly toxic. Because of the free electron pair on the N atom, the A. are basic, that is, they are able to add protons (they are proton acceptors in the Brönsted sense): $R_3N: + HX \rightarrow R_3N^+HX^-$.

Comparison of the pK_a values of aliphatic and aromatic A. reveals distinct differences; the aliphatic A. have higher pK_a values, and are thus more basic, than the aromatic A. The reason is that the free electron pair on the nitrogen atom of an aromatic A. is drawn into its π-electron system.

Gaseous aliphatic amines irritate the mucous membranes of the eyes and respiratory passages. When the skin is wetted with liquid alkylamines, it is severely burned. Poisoning by inhalation of higher concentrations can lead to elevation of blood pressure and temporary cramps. On the toxicity of aromatic amines, see Aniline.

Reactions. The reactions of various A. with nitrous acid are very important for many syntheses and also for characterization. Primary aliphatic A. are deaminated, forming alcohols, but primary aromatic A. form diazonium salts which can be converted to azo compounds by azo coupling around 0 °C. Secondary A. form yellow to orange nitrosoamines with nitrous acid. Tertiary aliphatic A. give unstable ammonium nitrites, and tertiary A. are converted under the same conditions to green, crystalline *p*-nitrosoarylamines. Some other important reactions of primary A. include the isonitrile reaction with chloroform and alkali hydroxide solution and the formation of azomethines with some carbonyl compounds, including aldehydes and ketones. A. can be converted to carboxylic amides by acylating reagents, and with hydrogen halides, such as hydrogen chloride, they form ionic compounds, the *amine hydrohalides* (e.g. *amine hydrochlorides*). Depending on the hydrocarbon group, these can also be called alkyl or aryl ammonium halides.

Analysis. A. can be identified chemically or by IR, NMR, or mass spectroscopy. The IR spectra of amines have absorption bands for the C-N valence vibration between 1020 and 1220 cm^{-1} for aliphatic A., and between 1250 and 1360 cm^{-1} for aromatic compounds. For primary and secondary A., the N-H valence vibrations absorb between 3300 and 3500 cm^{-1}, and the N-H deformation vibrations are between 1550 and 1650 cm^{-1}. In ^{1}H-NMR spectra, the signals for aliphatic NH groups are in the range of $\delta = 1$ to 2 ppm, and for aromatic A., between 2.6 and 4.7 ppm. A. with odd numbers of N atoms always have odd mass numbers. The occurrence of odd-numbered molecular ion peaks always indicates the presence of nitrogen. Aliphatic A. very often yield alkylamine cations as key fragments. Aromatic A. readily cleave off hydrogen cyanide.

Synthesis. Aliphatic A. are usually synthesized technically by alkylation of ammonia. The resulting mixture of amines can be separated by fractional distillation or by the Hinsberg separation (see). Some other methods of synthesis are the Gabriel synthesis (see), the Curtius degradation of acid azides (see), the Hoffman degradation of acid amides (see), the Ritter reaction (see) and the reduction of nitro compounds; this last method is the most important industrial source of primary aromatic amines.

Applications. A. are used as starting materials for the synthesis of pigments (azo and azomethine dyes), drugs (e.g. sulfonamides) and polyamide fibers.

Amine oxides, *N-oxides*: organic compounds with the general formula $R_3N \rightarrow O$. The bond between the N and O atoms is called a semipolar bond, because it is formally a combination of a single N-O covalent bond and an N^+O^- ionic bond. This type of bond can be symbolized as follows:

$$R_3N \longrightarrow \bar{O}| \quad \text{or} \quad R_3\overset{+}{N}\text{–}\bar{O}|^-$$

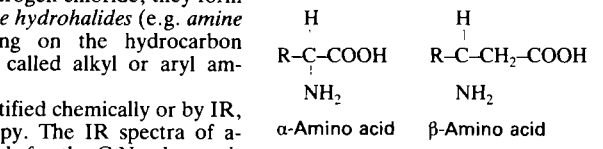
A. have very high dipole moments and high melting and boiling points, and can only be distilled in vacuum. They form salts with acids, with the general formula $(R_3N^+\text{-}OH)X^-$. Some of these compounds are used as chemotherapeutics.

A. are formed by oxidation of tertiary amines, e.g. by peroxides, or by oxidation of heterocycles with tertiary N atoms, e.g. pyridine and quinoline. A. can be converted back to the tertiary nitrogen bases by reaction with suitable reducing agents, such as triphenylphosphine. A. are used mainly for organic syntheses. For example, in the Cope reaction, alkenes are produced by thermolysis of aliphatically substituted A.

Amine resins: same as Amide resins (see).

Amine hydrochloride: see Amine.

Amino acids, *amino carboxylic acids*: organic acids in which one or more of the C-atoms in the hydrocarbon portion carries an amino group, $-NH_2$. Aliphatic A. are designated, α-, β-, γ-, ω-, etc., depending on the position of the NH_2 relative to the terminal COOH group.

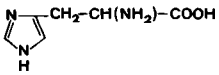
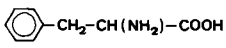
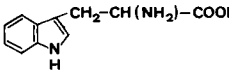
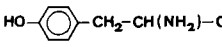


α-Amino acid β-Amino acid

If the NH_2 group is bound to a ring, the relative positions of the functional groups are indicated by the numbering of the ring atoms, e.g. 2-aminobenzoic acid. γ- and δ-A. are formed by heating cyclic lactams, for which a Lactam-lactim tautomerism (see) can be formulated. ε-A. and A. with greater distances between the NH_2 and a terminal COOH group can readily be converted to polyamides by intermolecular condensations; this is important in the synthesis of synthetic fibers, e.g. from ε-aminocaproic acid.

More than 500 A. are known to occur in nature; of these, the ***proteogenic A.*** (Table 1), which are incorporated into proteins, are of special significance. All are α-A., and with the exception of glycine, all are optically active. Only the L-configuration is found in proteins. D-A. are found in the cell walls of bacteria and various antibiotics, however.

Table 1. Proteogenic amino acids

Trivial name	Formula	m. p. (dec.) in °C	$[\alpha]_{25}^{D}$	IEP
Alanine Ala, A	$CH_3-CH(NH_2)-COOH$	297	+ 14.47 *c* = 10.0 in 6N HCl	6.00
Arginine Arg, R	$HN-CH_2-CH_2-CH_2-CH(NH_2)-COOH$ $HN=C(NH_2)$	238	+ 27.6 *c* = 2 in 6N HCl	11.15
Asparagine Asn, N	$H_2N-CO-CH_2-CH(NH_2)-COOH$	236	− 5.6 *c* = 2 in 5N HCl	5.41
Aspartic acid Asp, D	$HOOC-CH_2-CH(NH_2)-COOH$	271	+ 24.6 *c* = 2 in 6N HCl	2.77
Cysteine Cys, C	$HSH_2C-CH(NH_2)COOH$	240	+ 9.7 *c* = 8 in 1N HCl	5.02
Glutamine Gln, Q	$H_2N-OC-CH_2-CH_2-CH(NH_2)-COOH$	185	+ 31.8 *c* = 2 in 5N HCl	5.65
Glutamic acid Glu, E	$HOOC-CH_2-CH_2-CH(NH_2)-COOH$	202	+ 31.8 *c* = 2 in 5N HCl	3.22
Glycine Gly, G	H_2N-CH_2-COOH	292	–	5.97
Histidine His, H		287	− 39.2 *c* = 3.8 in water	7.47
Isoleucine Ile, I	H_3C-CH_2 $CH-CH(NH_2)-COOH$ H_3C	284	+ 40.6 *c* = 2 in 6N HCl	5.94
Leucine Leu, L	H_3C $CH-CH_2-CH(NH_2)-COOH$ H_3C	315	− 10.4 *c* = 2 in water	5.98
Lysine Lys, L	$H_2N-CH_2-CH_2-CH_2-CH_2-CH(NH_2)-COOH$	225	+ 25.9 *c* = 2 in 5N HCl	9.59
Methionine Met, M	$H_3C-S-CH_2-CH_2-CH(NH_2)-COOH$	283	+ 23.4 *c* = 5 in 3N HCl	5.74
Phenylalanine Phe, F		284	− 35.1 *c* = 2 in water	5.48
Proline Pro, P		222	− 85 *c* = 1 in water	6.30
Serine Ser, S	$HOH_2C-CH(NH_2)-COOH$	228	− 6.8 *c* = 10 in water	5.68
Threonine Thr, T	$H_3C-CHOH-CH(NH_2)-COOH$	253	− 28.6 *c* = 2 in water	5.64
Tryptophan Trp, W		281	− 32.1 *c* = 1 in water	5.89
Tyrosine Tyr, Y		290	− 7.3 *c* = 4 in 6N HCl	5.66
Valine Val, V	H_3C $CH-CH(NH_2)-COOH$ H_3C	315	+ 28.8 *c* = 3.4 in 6N HCl	5.96

IEP = isoelectrical point, *c* = concentration, N = normality

The general formula for a proteogenic A. is NH_2-CHR-COOH. The side chain, R, may be polar or nonpolar; the polar A. have acidic, neutral or basic side chains, and all are hydrophilic. The neutral, polar A. include serine, threonine, cysteine, asparagine, glutamine and tryptophan; the acidic A. are aspartic acid, glutamic acid and tyrosine; and the basic A. are lysine, arginine and histidine. The nonpolar A. are glycine and alanine; the hydrophobic A. are valine, leucine, isoleucine, proline, methionine and phenylalanine. The configurations of proteins in aqueous or nonaqueous media (e.g. cell membranes) are determined by the interactions of the A. side chains with the solvent and with each other.

A. are classified according to their metabolic fates as ***glucoplastic*** or ***ketoplastic***. Glucoplastic A. are degraded to C_4 dicarboxylic acids or succinic acid, and can be converted to carboydrates, while ketoplastic A. are degraded to ketone bodies, especially acetoacetate. A different system of classification is based on the ability of human or animal bodies to synthesize the proteogenic A.; ***essential A.*** are those which cannot be synthesized and are therefore required in the diet in the form of suitable Proteins (see) (Table 2). The requirements for essential A. depend on age and physiological state; growing and pregnant animals require more than non-pregnant adults. Ruminants obtain A. from the bacteria in their rumens, and can exist without other dietary protein if they have an adequate source of inorganic nitrogen (ammonium salts or urea).

Table 2. Human minimum daily requirement for essential amino acids

Amino acid (in g)		Amino acid in mg/kg body mass		
		Adults	Infants	Children (10–12 years)
Arg	1.8	.	.	.
His	0.9	.	28	.
Ile	0.7	10	70	30
Leu	1.1	14	161	45
Lys	0.8	12	103	60
Met	1.1	13	58	27
Phe	1.1	14	125	27
Thr	0.5	7	87	35
Trp	0.25	3.5	17	4
Val	0.80	10	93	33

Properties and reactions. The A., having NH_2 and COOH groups, are amphoteric, and their solutions are ampholytes. In the solid state and in solution, the A. have dipolar zwitterion structures, H_3N^+-CHR-COO^-, which accounts for their good solubility in polar solvents such as water and ammonia, and for their high melting points (200-300 °C). A. react with acids or bases by uptake or loss of protons:

$$H_3N^+\text{–CHR–COOH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_3N^+\text{–CHR–COO}^-$$

Cation Zwitterion

$$\underset{H+}{\overset{OH^-}{\rightleftharpoons}} H_2N\text{–CHR–COO}^-,$$

Anion

so the A. exist in acidic solutions as ammonium cations, and in alkaline solutions as carboxylate anions. In an electric field, the A. move toward the anode in an alkaline solution, and toward the cathode in acidic solution. At its isoelectric point (IEP), the pH at which it exists as a zwitterion, an A. does not migrate. At this point, the solubility of most A. in water is very low, because the hydrophilicity of the NH_2 and COOH groups is cancelled. This fact is useful in purification and recrystallization, and for electrophoretic separation of A. The acid-base behavior of all A. can be characterized by the pK values associated with their α-amino, α-carboxyl and side chain functions (K_1, pK_2, pK_3). The pK_1 values of the A. are lower than those of the comparable carboxylic acids; for example, the COOH group of glycine (pK_1 = 2.35) is much more acidic than that of acetic acid (pK = 4.76). Since the A. differ in their acidity, they can be conveniently separated by ion exchange chromatography. The titration curves of the A. have two regions of steep slope, in which they can be used as buffers. The acid-base behavior of the A. serves as a model for that of proteins and peptides, of which they are the components.

Chemically, the amino and carboxyl functions of the A. can react independently. Two reactions of practical significance are acylation to the very acidic acylamino acids, or esterification to amino acid esters, which act as strong organic bases.

Other characteristic reactions of the A. are N-alkylation, e.g. to N-methylamino acids, complex formation with metal ions, reaction with nitrous acid, which yields α-hydroxyacids upon N_2 cleavage, decarboxylations to Biogenic amines (see) and transaminations, in which the NH_2 group of one A. is reversibly transferred to the α-C of an α-ketoacid. The amide linkage of A. to form peptides and proteins is extremely important.

Analytical. Qualitative analysis of A. depends mainly on chromatographic separation and subsequent identification by a color reaction. The *ninhydrin reaction* produces a blue-violet pigment (absorption maximum at 570 nm) by reaction of ninhydrin (2,2-dihydroxy-IH-indene-1,3(2H)-dione) with the A. *Fluorescamine*, 4-phenyl[furan-2H(3H)-1'-phthalane]-3,3'-dione, reacts with the A. to produce highly fluorescent compounds which can be detected in the nanomolar range at 336 nm. Some other highly sensitive reagents for A. are 2,4,6-trinitrobenzenesulfonic acid, Folin's reagent (1,2-naphthoquinone-4-sulfonic acid) and 4,4'-tetramethyldiaminodiphenylmethane (TDM). Intensely fluorescent amino acid derivatives are formed with o-phthalaldehyde in the presence of reducing agents, or with dansyl chloride (5-dimethylaminonaphthalinesulfonyl chloride).

Mixtures of A. are separated by electrophoresis, paper and thin-layer chromatography; for quantitative determination, ion exchange chromatography is used. The first automated amino acid analyser developed by Spackman, Moore and Stein required 24 h for analysis of a protein hydrolysate; modern machines need only 45 min, and the limit of detection lies in the picomole range.

Production. A. can be obtained by isolation from protein hydrolysates, by biotechnological means, or by chemical synthesis. The classic method for isola-

tion from proteins begins with hydrolysis of the protein in hydrochloric acid for 12 to 72 h; tryptophan is completely destroyed and serine/threonine are partially degraded (up to 10%) by this treatment. Cysteine and tyrosine are precipitated from the hydrolysate by neutralization, and the A. remaining in the mother liquor are separated by chromatography on synthetic resin ion exchangers or by extraction. The enzymatic hydrolysis of proteins by bacterial proteases is becoming more important.

All proteogenic A. can now be produced by biotechnological means, either by microbial production (fermentation), using mutants which produce more of a particular A. than they need, or biotransformation. The enzymes for biotransformations are usually attached to a solid carrier, and the reagents flow past them. They carry out specific steps in the synthesis, usually those for which enantiomeric selectivity is required. Glutamic acid (see) is now produced by fermentation, while the enzymatic synthesis of Lysine (see) is an example of biotransformation.

The most important methods of chemical synthesis of A. are 1) reaction of halocarboxylic acids with ammonia, e.g. for glycine; 2) the Strecker synthesis (see); and 3) ***malonic ester synthesis***: malonic ester reacts with nitrous acid to form oximinomalonic ester, which is converted to formyl- or acetaminomalonic ester by reduction and acylation of the free amino group. The side chain of the A. is introduced by reaction with aldehydes or alkyl halides. This complicated synthesis is used for only a few A., e.g. asparagine and tryptophan.

Since the chemical synthesis of A. always produces DL compounds, the enantiomers must be separated at the end of the synthesis. The industrially useful methods are: a) spontaneous crystallization of one enantiomer from the supersaturated solution of amino acid salts; b) reaction with optically active compounds to produce diasteriomeric salts, which can be fractionally crystallized; and c) the enantioselective hydrolysis of amino acid derivatives (acetyl- and chloroacetylamino acids or amino acid esters) by immobilized acylases or esterases.

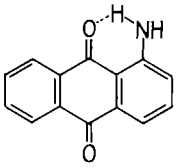
The separation of enantiomers is not needed in asymmetric synthesis of A., e.g. by the Strecker synthesis with optically active amines, or by enantioselective hydrogenation of α,β-dehydroamino acids, R-CH=C(NH_2)COOH, in the presence of optically active Wilkinson catalysts. Such methods produce A. of relatively high optical purity. For example, an industrial synthesis of DOPA (3,4-dihydroxyphenylalanine) yields 97% L- and 3% D-DOPA.

The world production of A. in 1980 had passed the 500,000 ton level. The largest amount was of L-glutamic acid (340,000 t), followed by DL-methionine (120,000 t) and lysine (34,000).

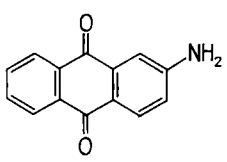
Applications. A. are used in large amounts as flavorings in foods (monosodium glutamate, aspartic acid, cystine, alanine and glycine), as infusion solutions for intravenous feeding (all proteogenic A.), for supplementation of foods (e.g. rice, maize, wheat flour) and feeds (e.g. chicken feed), for supplementation of the diets of domestic animals (lysine, methionine, threonine), as additives to skin cremes, shampoos and other cosmetics (cysteine derivatives) and, in small amounts, as vulcanization promoters, additives for galvanic baths and corrosion inhibitors. In organic synthesis, A. are used as starting materials for synthesis of peptides, pharmaceuticals and pesticides, and, in increasing amounts, as chiral components and intermediates for synthesis of optically active compounds and nitrogen heterocycles.

Aminoanisoles: same as Ansidines (see).

Aminoanthraquinones: derivatives of anthraquinone in which one or more aromatic H atoms are replaced by amino groups, -NH_2. A. are colored compounds which are only slightly soluble in water, but dissolve readily in alcohol and ether. In A. with primary or secondary amino groups in positions 1, 4, 5 or 8, relatively strong hydrogen bonds are formed, as in hydroxyanthraquinones. A. are synthesized mainly by reduction of nitroanthraquinones or anthraquinone sulfonic acids with ammonia. They are used as starting materials for synthesis of dyes.



1-Aminoanthraquinone



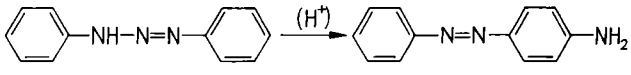
2-Aminoanthraquinone

4-Aminoazobenzene, ***aniline yellow***: yellow leaflets or needles; m.p. 127 °C, b.p. > 360 °C. A. is only slightly soluble in water, but dissolves readily in alcohol, ether, benzene or chloroform. It is synthesized by reaction of benzene diazonium salts with aniline hydrochloride and rearrangement of the primary product, diazoaminobenzene. It may also be synthesized by direct reaction of aniline hydrochloride with diazoaminobenzene. The ***diazoamino-aminoazo rearrangement*** is an intermolecular process which can be formulated as follows:

$$C_6H_5\text{–}NH\text{–}N{=}N\text{–}C_6H_5 \xrightarrow{+H^+} C_6H_5\text{–}\overset{+}{N}H_2\text{–}N{=}N\text{–}C_6H_5 \longrightarrow$$

$$C_6H_5\text{–}NH_2 + \overset{+}{N}{=}\overset{+}{N}\text{–}C_6H_5 \xrightarrow[-H^+]{} C_6H_5\text{–}N{=}N\text{–}C_6H_5\text{–}NH_2.$$

The diazonium ion can be detected by trapping reactions, and this confirms the intermolecular nature of the rearrangement.



Diazoaminobenzene

4-Aminoazobenzene

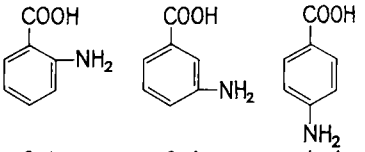
In the presence of strong mineral acids, A. forms steel-blue, stable salts; there is also a violet form which is less stable. A. is used as an intermediate in the production of azo dyes, which are used mainly as dispersion dyes.

5-Aminobarbituric acid: same as Uramil (see).

Aminobenzene: same as Aniline (see).

4-Aminobenzenesulfonic acid: same as Sulfanilic acid (see).

Aminobenzoic acids: three structural isomers which are slightly soluble in cold water, and somewhat more soluble in hot water and alcohol. Because of their amphoteric nature, they form salts with either strong bases or mineral acids. A. can be sublimed in vacuum without decomposition. ***o-*** or ***2-aminobenzoic acid, anthranilic acid*** forms light yellow leaflets; m.p. 146-147 °C. The solutions give a blue fluorescence. 2-Aminobenzoic acid is found as the methyl ester in many plants, such as jasmine and bergamotte. It is synthesized industrially, mainly by Hofmann degradation of phthalimide. It can also be made by reduction of 2-nitrobenzoic acid, reaction of 2-chlorobenzoic acid with ammonia in the presence of copper salts, or by intramolecular redox reaction of 2-nitrotoluene. 2-Aminobenzoic acid is used in the synthesis of indigo, thioindigo, azo dyes, perfumes and salves for burns. It is also used as an indicator for many metals. ***m-*** or ***3-aminobenzoic acid*** forms pale yellow crystals, m.p. 174 °C. It is made technically by reduction of 3-nitrobenzoic acid. 3-Aminobenzoic acid is an important intermediate for the synthesis of azo dyes. ***p-*** or ***4-aminobenzoic acid***, abb. ***PABA*** is a colorless, crystalline compound; m.p. 186-187 °C. It is found in free or bound form in yeasts, enzymes and folic acid. It is essential for the growth of many microorganisms, including lactic acid bacteria, streptococci, staphylococci and pneumococci. It acts as an antagonist to sulfonamides used as antibiotics. In the human body, it is detoxified by formation of *N*-acetylaminobenzoic acid. 4-Aminobenzoic acid is made industrially by reduction or hydrogenation of 4-nitrobenzoic acid. It is an intermediate in the synthesis of azo dyes, folic acid and a number of esters used as local anesthetics; it is also the active ingredient in sunblocking skin creams used to prevent sunburn.



2-A. 3-A. 4-A.

Aminobutanes: see Butylamines.

γ-Aminobutyric acid: see Biogenic amines, Table.

4-Aminobutyric acid lactam: same as Pyrrolidone (see).

ε-Aminocaproic acid: H_2N-$(CH_2)_5$-COOH, a white, crystalline substance; m.p. 202-203 °C. ε-A. is soluble in water and insoluble in ether. It is used as an antifibrinolytic and is an intermediate in the polymerization of ε-Caprolactam (see) to make polyamide fibers.

Aminocarboxylic acids: same as Amino acids (see).

Aminochromes: see Catecholamines.

Amino compounds: see Amines.

Aminocyclitol antibiotics: a group of antibiotics in which a base-substituted cyclitol is glycosidically bound to two or three monosaccharides, usually amino sugars. A. are found in actinomycetes (*Streptomyces, Micromonospora*). The therapeutically important A. are derived from streptomycin, neomycin and kanamycin. The streptomycin type A. have streptidin(1,3-deoxy-1,3-diguanidino-myo-inositol) as their cyclitol. The other two types of A. contain 2-deoxystreptamine (1,2-diamino-1,2,3-trideoxy-myo-inositol).

Aminocyclohexane: same as Cyclohexylamine (see).

p-Amino-N,N-diethylaniline: same as *N,N*-Diethyl-p-phenylenediamine.

5-Amino-2,3-dihydrophthalazine-1,4-dione: same as Luminol (see).

5-Amino-1,4-dihydroxyphthalazine: same as Luminol (see).

Aminodimethylbenzene: same as Xylidine (see).

Aminoacetic acid: same as Glycine (see).

Aminoethane: same as Ethanolamine (see).

2-Aminoethanethiol: same as Cysteamine (see).

Aminoethyl alcohols: same as Ethanolamines (see).

4-(2-Aminoethyl)pyrocatechol: same as Dopamine (see).

β-Aminoethylmercaptan: same as Cysteamine (see).

Aminoformic acid: same as Carbamic acid (see).

Aminoglycoside antibiotics, *oligosaccharide antibiotics*: a group of antibiotics in which glycosidic aminosugars and monosaccharide components are linked to each other and/or to basic cyclohexane derivatives containing multiple hydroxyl groups. The A. have a broad action spectrum and are used mainly against infections by gram-negative bacteria. However, they are relatively toxic. Resistance can be developed by enzymatic acetylation of the amino groups or phosphorylation and adenylation of the hydroxyl groups. (Adenylation is the transfer of an adenosine 5'-phosphate group to the molecule.) The A. include streptomycin, neomycin, paromomycins, kanamycins and gentamycins.

Amino group: in the narrow sense, the group $-NH_2$, which is the functional group in all primary amines and amides. In the wider sense, the term includes mono- and disubstituted nitrogen derivatives of the type RHN- and R_2N-, such as the methylamino group $(CH_3)HN$- or the ethylmethylamino group, $(C_2H_5)(CH_3)N$-.

1-Aminohexane: same as Hexylamine (see).

6-Aminohexanoyl lactam: same as ε-Caprolactam (see).

Aminolysis: the reaction corresponding to hydrolysis in which the reactive substituent in a compound is replaced by an amine group. For example, the halogen atom in a haloalkalne can be replaced by an amino group. Similarly, carboxylate esters can be converted to amides. If A. is carried out in ammonia, the reaction is called ***ammonolysis***, e.g. $C_2H_5Cl + 2\ NH_4 \rightarrow C_2H_5NH_2 + NH_4Cl$.

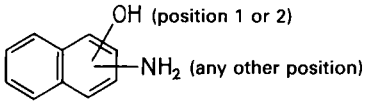
Aminomethane: see Methylamine.

Aminomethylation: see Mannich reaction.

Aminomethylpropanes: two structurally isomeric amino derivatives of 2-methylpropane; see Butylamines.

Aminonaphthalenes: same as Naphthylamines (see).

Aminonaphthols: 14 isomeric aminohydroxynaphthalenes. These compounds form colorless crystals; they are amphoteric and dissolve in acids and alkaline solutions. They are slightly soluble in water, and readily soluble in alcohol and ether. They are usually synthesized by reduction of the corresponding nitronaphthols, or by alkaline hydrolysis of aminonaphthalenesulfonic acids. A. are used as couplers for dyes.



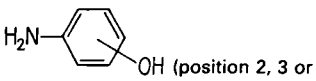
Aminonitrobenzenes: same as Nitroanilines.

Aminopeptidases: a class of exopeptidases (see Proteases) which catalyse the cleavage of the amino-terminal amino acid from a polypeptide chain. A. are large proteins consisting of several subunits (M_r up to 330,000), and most of them have divalent metal ions as effectors. The best known is ***leucine aminopeptidase***, which can be isolated in crystalline form from bovine eye lenses, kidneys or the mucous membrane of the small intestine. A. are used for the step-wide degradation of peptide chains (sequence analyses). Peptide bonds to proline are not cleaved by A.

Aminophenazone: see Pyrazolones.

Aminophenetols: same as Phenetidines (see).

Aminophenols: phenols with one or more amino groups on the aromatic ring. A. are amphoteric, but the basic characteristics dominate. The most important A. are 2-A., 3-A. and 4-A.



2-Aminophenol (o-aminophenol) forms colorless leaflets or needles; m.p. 174 °C, sublimation at 153 °C and 1.47 kPa. It is nearly insoluble in cold water, but somewhat more soluble in alcohol and ether. It is synthesized by reduction of 2-nitrophenol with iron in weakly acidic solution, or by reduction of nitrobenzene via phenylhydroxylamine. This intermediate rearranges under the acidic reaction conditions to 2- and 4-A. 2-A. is used in the production of pigments, drugs and hair dyes.

3-Aminophenol (m-aminophenol), colorless, hexagonal prisms; m.p. 123 °C, b.p. 164 °C at 1.47 kPa. It is slightly soluble in water, and readily soluble in alcohol and ether. 3-A. is obtained mainly by the reaction of alkali hydroxides with 3-aminobenzenesulfonic acid or from resorcinol and ammonia in the presence of catalysts. It is used to synthesize the important drug, aminosalicylic acid, and rhodamine dyes.

4-Aminophenol (p-aminophenol), colorless leaflets; m.p. 186-187 °C, sublimation at 180 °C and 360 Pa. It is nearly insoluble in water, somewhat soluble in alcohol, and soluble in chloroform and benzene. The most important method of synthesis of 4-A. is the reduction of 4-nitrophenol with iron in weakly acidic solution or the reduction of nitrobenzene via phenylhydroxylamine. 4-A. is used as a photographic developer. It is also used in the synthesis of modified photodevelopers, sulfur and azo pigments, and drugs.

Aminophenyl ethyl ether: same as Phenetidine (see).

Aminophenyl methyl ether: same as Anisidine (see).

3-Aminophthaloyl hydrazide: same as Luminol (see).

Aminophyllin: see Theophyllin.

Amino plastics: see Amide resins.

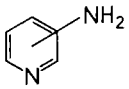
Aminopropanols, ***propanolamines***: aliphatic compounds with an amino and a hydroxyl group in the molecule. They are colorless liquids with fishy odors and are soluble in water and alcohol. They display the chemistry of both amines and alcohols, and form salts with acids. Of the five possible isomeric A. with primary amino groups, two are used extensively in industry. ***3-Aminopropan-1-ol***, $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$, b.p. 187-188 °C, n_D^{20} 1.4617., is synthesized by catalytic hydrogenation of ethylene cyanohydrin in the presence of ammonia. It is used to make drugs, dyes, synthetic resins and soaps. ***1-Aminopropan-2-ol (isopropanolamine)***, $CH_3\text{-}CH(OH)\text{-}CH_2\text{-}NH_2$, m.p. 1.9 °C, b.p. 159.2 °C, n_D^{20} 1.4478, is a degradation product of vitamin B_{12}. It is synthesized by reaction of propylene oxide with ammonia under pressure. 1-Aminopropan-2-ol is used to synthesize dyes, soaps, drugs and pesticides.

In addition to *N*-unsubstituted A., there are many *N*-mono- and *N*-dialkyl compounds of this type which are synthesized and utilized in industry.

Aminopropionic acid: same as Alanine (see).

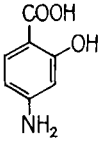
6-Aminopurine: same as Adenine (see).

Aminopyridine: an amino derivative of pyridine. ***2-Aminopyridine*** has colorless, crystalline leaflets, m.p. 57-58 °C, b.p. 204 °C. It is soluble in water, alcohol and ether, and is a base. When heated with 2-chloropyridine in the presence of zinc chloride, it forms di-α-pyridylamine. 2-Aminopyridine is obtained by the Čičibabin reaction (see). It is used in industry in the production of pigments, sulfonamides and antihistamines. ***3-Aminopyridine*** forms yellowish crystalline leaflets, m.p. 65 °C, b.p. 252 °C. It is synthesized from nicotinamide by Hofmann degradation. ***4-Aminopyridine*** forms yellowish needles; m.p. 158-159 °C, b.p. 180 °C at 1.74 kPa. It is formed by decarboxylation of 4-aminopicolinic acid. ***2,6-Diaminopyridine*** forms colorless crystals; m.p. 121-122 °C, b.p. 148-150 °C at 0.67 kPa. It is obtained by heating pyridine with two moles sodium amide in cumene. Further amination of 2-aminopyridine also yields 2,6-diaminepyridine. It is very interesting that A., in contrast to pyridine itself, readily undergo electrophilic reactions. For example, nitration yields 2-amino-3-nitropyridine, which can be hydrogenated to form 2,3-diaminopyridine. A. are used as intermediates in the production of dyes.



5-Aminopyrimidine-2,4,6-triol: same as Uramil (see).

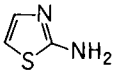
p-Aminosalicylic acid, abb. ***PAS***: a compound used as a tuberculostatic. It forms white crystals which are soluble in ethanol but only slightly soluble in water or ether; m.p. 150-151 °C. It decomposes by decarboxylation to form 3-aminophenol, or by oxidation to colored products. It is synthesized by the Kolbe-Schmitt synthesis from the sodium salt of 3-aminophenol and CO_2. High doses of the sodium or potassium salt are used in therapy. A. acts as an antimetabolite of *p*-aminobenzoic acid.



α-Aminosuccinic acid: same as Aspartic acid (see).

Aminosugars: monosaccharides in which one or more alcoholic hydroxyl groups have been replaced by amino groups. The free A. are relatively strong bases, and are not very stable. In nature, A. are always bound glycosidically; they are especially plentiful in animals and microorganisms. With the exception of a few basic A.-glycosides in microorganisms, which include the Aminoglycoside antibiotics (see), the amino group of the A. is always amidated as N-acetyl or, less commonly, as N-sulfuryl. Neither group is basic. The most abundant A. in animals are derivatives of 2-amino-2-deoxyhexoses, such as D-Glucosamine (see), D-Galactosamine (see) and D-mannosamine. These A. are components of polysaccharides, e.g. of Chitin (see), Mucopolysaccharides (see), Blood group substances (see) and many glycoproteins. In addition to 2-amino-2-deoxyhexoses, microorganisms also contain methylated A. and 3-amino-2-deoxy-, 6-amino-6-deoxy- and 2,6-diamino-2,6-dideoxysugars. Among other functions, A. serve as components of bacterial cell walls (see Murein). Another important A. is Neuraminic acid (see).

2-Aminothiazole: a heterocyclic compound forming yellow crystals with m.p. 93 °C, b.p. 140 °C at 1.47 kPa. A. is readily soluble in hot water, but less soluble in alcohols and ethers. Like an aromatic amine, it can be diazotized; it also couples with diazonium salts to form azo dyes. It is obtained by reaction of chloroacetaldehyde with thiourea, or better, from vinyl acetate and thiourea in the presence of sulfuryl chloride. A. is used as a starting material for synthesis of the sulfonamide sulfathiazole.



Aminotoluene: same as toluidine.

Aminotransferases, ***transaminases***: enzymes which reversibly transfer the α-amino group of an amino acid to a 2-oxoacid. Aspartate aminotransferase (known in medicine as ***glutamic-oxaloacetic transaminase, GOT***) and alanine aminotransferase (known in medicine as ***glutamic-pyruvic transaminase, GPT***) are diagnostically useful because their serum concentrations rise in certain illness (cardiac infarction, hepatitis).

Aminoxylenes: same as Xylidines (see).

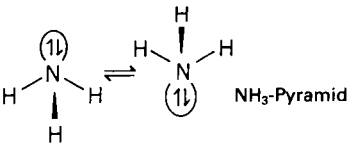
Amitriptyline: see Dibenzodihydrocycloheptadienes.

Amitrol: see Herbicides.

Ammine complexes: complexes in which ammonia, NH_3, is present as a ligand. Chromiacs (see) and Cobaltiacs (see) are important examples of this type of compound.

Ammonia: NH_3, a colorless gas with a characteristic and very strong odor; M_r 17.03, m.p. - 77.4 °C, b.p. - 33.35 °C, crit. temp. 132.5 °C, crit. pressure, 11.25 MPa, crit. density, 0.235, density of liquid A. at - 34.4 °C, 0.683, at 0 °C, 0.639; vapor pressure at 0 °C, 0.438 MPa, at 30.0 °C, 1.19 MPa; heat of evaporation of the liquid at - 33.35 °C, 1372.0 kJ kg^{-1}, at 0 °C, 1264.3 kJ kg^{-1}, and at 32.2 °C, 1137.3 kJ kg^{-1}. Solid A. consists of colorless, cubic crystals.

Properties. The ammonia molecule is pyramidal, with an H-N-H angle of 107.3°. From this one can conclude that the N atom is largely sp^3 hybridized. It sits at the center of a tetrahedron with protons on three vertices; the free electron pair is oriented toward the fourth vertex (Ψ-tetrahedral molecule). The NH_3 pyramid is not stable; even at low temperatures, it undergoes rapid inversion in which the N atom passes through the plane of the three H atoms. The energetic barrier to inversion is 24.8 kJ mol^{-1}. The high polarity of the NH_3 molecule and the formation of strong hydrogen bonds cause liquid A. to be highly associated (dielectric constant at - 50 °C is 22.7). This is the reason for the unusually high boiling point and the high enthalpy of evaporation of A.



As a result of its molecular structure, A. is able to act either as a donor or acceptor molecule, that is, it can solvate either anions or cations. This gives liquid A. solvent properties similar to those of water. Many inorganic and organic compounds are soluble in A., including many halides, pseudohalides, nitrites and nitrates, sulfur, selenium, phosphorus, alcohols, aldehydes, phenols and esters. Liquid A., like water, undergoes autoprotolysis: $2\ NH_3 \rightleftharpoons NH_2^- + NH_4^+$. Thus there is a neutralization in the ammono system, consisting of the combination of amide and ammonium ions to A., which is comparable to neutralization in water. An example is the reaction $NH_4I + NaNH_2 \rightarrow 2\ NH_3 + NaI$. Alkali metals and calcium, strontium and barium dissolve in liquid A., forming dark blue solutions. The electrical conductivity and paramagnetism of these solutions are due to the presence of solvated electrons:

$$M \xrightarrow{\text{liq. } NH_3} M^+ + [e(NH_3)_x]^-.$$

A. dissolves aggressively in water. At 0 °C, 90.7 g A. dissolve in 100 ml water; this is equivalent to 117.6 l gaseous A. At 100 °C, 7.4 g A. dissolves in 100 ml water. The enthalpy of solution of gaseous A. at 25 °C is 30.64 kJ mol^{-1}. The concentration of an aqueous NH_3 solution can be determined directly from its density:

D	0.880	0.900	0.920	0.940	0.960	0.980	0.990
% NH_3	34.35	27.33	20.88	14.88	9.34	4.27	1.89

In water, most dissolved A. is molecular. However, due to the ability of A. to accept protons, a slight amount of protolysis occurs: $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$ ($pK_B = 4.75$). The aqueous solution is thus basic. The basic character of A. is also expressed by its ability to form ammonium salts with strong acids. In the presence of strong bases, A. is released from ammonium salts. For example, $NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$. A. can act as an acid with respect to very strong bases, such as organometal compounds or ionic hydrides, and is converted to its corresponding base, the amide ion NH_2^-. Amides are also formed by the action of electropositive metals on A. at high temperatures, e.g. $Na + NH_3 \rightarrow NaNH_2 + 1/2\ H_2$. The amides M^INH_2 can be converted to metal imides, M^I_2NH and metal nitrides, M^I_3N, by increasing the temperature.

A. is stable at normal temperatures, but decomposes into its elements when heated in the presence of certain catalysts: $2\ NH_3 \rightleftarrows N_2 + 3\ H_2$, $\Delta H = 92.5$ kJ mol^{-1}. A. burns in pure oxygen, mainly to nitrogen and water: $2\ NH_3 + 3/2\ O_2 \rightarrow N_2 + 3\ H_2O$. Mixtures of A. and oxygen are explosive in the concentration range of 13.5 to 82 vol. % A., and A.-air mixtures in the range of 15.5 to 28 vol. % A. If the combustion takes place in the presence of platinum or platinum/rhodium catalysts, nitrogen monoxide is formed: $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$, $\Delta H \approx -900$ kJ mol^{-1}. This reaction is the basis of the Ostwald process for synthesis of nitric acid. Due to its free electron pair, A. is a good complex ligand in coordination compounds, and a strong nucleophile in ammonolysis.

Both liquid ammonia and its aqueous solutions are irritating to the skin and mucous membranes. The eyes are especially at risk. If ammonia gets into the eyes, they must immediately be rinsed with large amounts of water.

1.5 to 2.5 g m^{-3} air causes death within 30 to 60 minutes. Inhalation for a short period can cause burns and lead to inflamation of the respiratory passages and lung edema. In this case, complete quiet and inhalation of water and glacial acetic acid vapors are recommended. When aqueous ammonia is swallowed, acid solutions (acetic, tartaric or citric acid) should be administered.

Analytical. A. is detected qualitatively by formation of the blue $[Cu(NH_3)_4]$ complex or by Nessler's reagent (see); it is determined quantitatively by distilling it out of an alkaline aqueous solution, absorbing it in acid and back titrating the excess acid. A. can also be determined with NH_3-sensitive electrodes.

Occurrence. A. is the biological degradation product of many organic nitrogen compounds, and occurs in nature, usually in the form of ammonium salts, as a result of decay of organic matter. A few minerals contain small amounts of A.

Production. Today, nearly all A. is synthesized by direct combination of nitrogen and hydrogen on the principle of the *Haber-Bosch process*. The processes based on this method differ only in the means of production and purification of the synthesis gas, the choice of reaction conditions (such as pressure and temperature), the catalysts and the technical realization of the individual steps of the process. The reaction $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$, $\Delta H = -92.5$ kJ mol^{-1} requires the input of large amounts of activation energy, due to the high dissociation enthalpy of the N_2 molecule. However, because it is an exothermal reaction, the amount of heat which can be applied is limited; as the temperature rises, the equilibrium position is shifted to the left. For this reason, catalysts have been developed which permit economically useful rates at a reaction temperature of 400 °C. (The catalysts are iron oxides with small amounts of the oxides of aluminum, calcium, potassium, magnesium, titanium, etc. as promotors; after reduction by hydrogen, the iron oxide is converted to the active α-form.)

The figure is a diagram of an ammonia plant. There are two types of reactor: cylinders filled with catalyst are cooled over their entire length, while layered reactors contain 5 to 10 layers of catalyst and are cooled by input of cold gas. Before it enters the reactor, the synthesis gas is heated to the working temperature of the catalyst (400-500 °C) by heat exchange with the reacted gas. After the reacting mixture passes each layer of catalyst, cold gas is added to cool it to the appropriate temperature. After about the 5th to 10th catalytic layer has been passed, the gas has reached the equilibrium concentration. It leaves the reactor and passes through a cooling vat, a heat exchanger to preheat the synthesis gas, and a water cooler. At this point, part of the A. precipitates. The remainder is removed from the circulation by a low-temperature cooler filled with A. The unreacted gas is returned to the reactor with fresh synthesis gas (with a ratio of N_2 to H_2 of 1:3). A compressor in the circulation compensates for the loss of pressure. Part of the flow is continuously decompressed, to prevent accumulation of inert gases (argon and methane) in the circulating gas. Argon can be extracted from these decompression gases.

Other possibilities for A. synthesis are fixation with organometallic complexes, biochemical fixation and conversion of nitrogen to nitrogen monoxide in a plasma. A. can also be extracted from coking plant wash water. In future, the plasma methods may become significant in connection with nuclear energy. In the laboratory, A. is produced by the reaction of strong bases with ammonia salts.

A. is commercially available in steel bottles, or as a 25 to 35% solution in water (***ammonium hydroxide***).

Applications. A. is a raw material for nearly all industrial syntheses of nitrogen compounds. The greatest fraction of the world production is used to make nitrogen fertilizers, especially urea and ammonium sulfate; liquid A. is also applied directly. A. is used in the production of soda, nitric acid, various

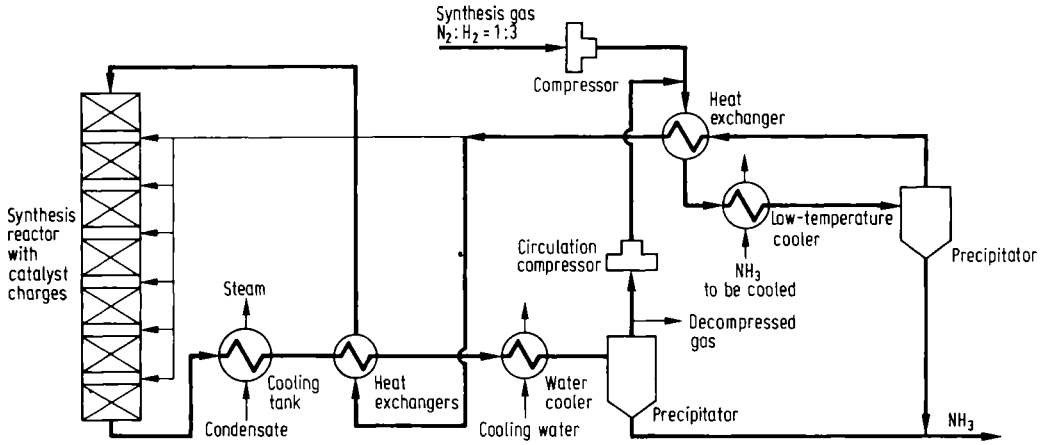


Diagram of an ammonia synthesis plant.

ammonium salts, sodium cyanide, hydrogen cyanide, hydrazine, nitriles, amines, amide resins, synthetic fibers, dyes, explosives, etc. It is used in refrigeration and in metallurgy (for nitro hardening). Ammonium hydroxide is used in bleaching and dyeing, and generally as a cheap base.

Ammonia resin: see Latex resins.

Ammonia-soda process: see Soda.

Ammonites: see Ammonium nitrate explosives.

Ammonium acetate: CH_3COONH_4, a colorless, hygroscopic mass, which is readily soluble in water and ethanol; M_r 77.08, density 1.17, m.p. 114 °C. A. is synthesized by reaction of glacial acetic acid with ammonia or ammonium carbonate. It is used to preserve meat and in dyeing.

Ammonium alum: same as ammonium aluminumsulfate.

Ammonium aluminumsulfate, ***ammonium alum***: $NH_4Al(SO_4)_2 \cdot 12H_2O$, colorless, water-soluble, cubic crystals, M_r 453.33, density 1.64, m.p. 93.5 °C. A. is used in water purification, paper-making, tanning, flame-retardants, caustics and in medicine as an astringent.

Ammonium carbamate: $H_2N\text{-}CO\text{-}O^- NH_4^+$, the ammonium salt of carbamic acid. A. forms colorless, water-soluble rhombic crystals which smell like ammonia. In aqueous solution it hydrolyses at 60 °C, forming ammonium carbonate, which readily decomposes to ammonia and carbon dioxide. A. is formed by heating dry ammonia with carbon dioxide. It is an intermediate in the synthesis of Urea (see), and is used as a cleanser, caustic and neutralizing reagent. One type of baking powder is a mixture of A. with ammonium hydrogencarbonate.

Ammonium carbonate: $(NH_4)_2CO_3 \cdot H_2O$, colorless, water-soluble, cubic crystals; M_r 114.10. A. smells of ammonia even at room temperature, and at 58 °C, it decomposes completely into NH_3, CO_2 and H_2O. It is synthesized by reaction of carbon dioxide with ammonia in aqueous solution: $2\ NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$, or by heating a mixture of ammonium sulfate and calcium carbonate: $(NH_4)_2SO_4 + CaCO_3 \rightarrow CaSO_4 + (NH_4)_2CO_3$. The A. sublimes off, together with the ammonium hydrogencarbonate and ammonium carbamate byproducts. It is used in dyeing and as a CO_2 source in fire extinguishers.

Ammonium carbonate group: see Analysis.

Ammonium chloride: NH_4Cl, colorless, cubic crystals with a bitter taste; M_r 53.49, density 1.527, soluble in water and ethanol. The aqueous solution is slightly acidic. As the temperature is increased, A. becomes volatile, due to thermal dissociation into ammonia, NH_3, and hydrogen chloride, HCl. At 340 °C, it sublimes rapidly. This process, like the combination of NH_3 and HCl to form A., depends on the presence of catalytic amounts of water. A. melts under pressure at 520 °C. It is obtained by adding hydrochloric acid to aqueous ammonia solutions, or to the gas scrub water from coking plants. A. is a byproduct of Soda (see) production by the Solvay process. It was formerly used as the nitrogen component of combination fertilizers. It is still used in dyeing, tanning leather and making galvanoplastics, iron-rust cement and cold mixtures. Its use in soldering, zinc plating and tinning is based on its ability to react with metal oxides and form volatile chlorides, and thus to clean the metal surface. A. is used as an electrolyte in dry batteries, and as an expectorant in medicine.

Ammonium cyanate: NH_4OCN, colorless crystals, soluble in ethanol and water, M_r 60.06, D. 1.342. The salt can be made by neutralization of cyanic acid with ammonia; above 60 °C it is converted to urea: $NH_4OCN \rightarrow H_2N\text{-}CO\text{-}NH_2$. This rearrangement was first carried out in 1828 by Wöhler. At the time, it was believed by many that natural products could not be synthesized outside living organisms; this synthesis was taken as proof to the contrary.

Ammonium hydrogencarbonate, ***primary ammonium carbonate***, formerly, ***ammonium bicarbonate***: NH_4HCO_3, colorless, water-soluble powder or rhombic or monoclinic crystals; M_r 79.06, density 1.58. Even at 40 to 60 °C, A. decomposes into ammonia, carbon dioxide and water. If the aqueous solution is heated, carbon dioxide escapes and forms neutral ammoniumcarbonate: $2\ NH_4HCO_3 \rightarrow (NH_4)_2CO_3 + CO_2 + H_2O$. It is made by passing carbon dioxide through aqueous ammonia solution.

In the synthesis of Soda (see) by the Solvay process, A. is formed as a byproduct. It is used as an additive for cattle feed, and as a component of baking powders (see Hartshorn salt).

Ammonium fluorides: ***Ammonium fluoride***, NH_4F, colorless, water-soluble, hexagonal crystals; M_r 37.04, density 1.009. NH_4F is formed as a sublimate when a mixture of ammonium chloride and sodium fluoride is heated. In aqueous solution, it splits off ammonium, and after evaporation of the solution, the rhombic or tetragonal crystals of ***ammonium hydrogenfluoride***, NH_4HF_2, M_r 57.04, density 1.50, m.p. 125.6 °C, are left. NH_4HF_2 can also be obtained by neutralization of hydrofluoric acid with ammonia. Among other things, it is used to etch glass and metal and as a disinfectant in breweries and distilleries.

Ammonium hexachlorostannate: same as Pink salt (see).

Ammonium hydrogensulfate, formerly ***ammonium bisulfate***, NH_4HSO_4, colorless, water-soluble, rhombic crystals, M_r 115.11, density 1.78, m.p. 146.9 °C. A. is used as an acidic condensation reagent in organic synthesis.

Ammonium hydrogensulfide: NH_4HS, colorless, poisonous rhombic crystals, readily soluble in water; M_r 51.11, density 1.17. A. decomposes even at room temperature into ammonia, NH_3, and hydrogen sulfide, H_2S. The aqueous solutions are alkaline; they are obtained by saturation of aqueous ammonia with hydrogen sulfide. Conversion of A. into a neutral ammonium sulfide, $(NH_4)_2S$, for example by addition of a second equivalent of NH_3, does not occur, because the ammonium ion, NH_4^+, is a stronger acid than hydrogen sulfide, HS^-, by a factor of about 10^4. The aqueous solution of A. is used mainly for separation of cations in qualitative analysis.

Ammonium hydroxide: a term used for aqueous ammonia solutions; it is a misnomer, because the compound NH_4OH does not exist (see Ammonia). The solid compound which can be made at low temperatures from NH_3 and H_2O (melts at - 77 °C) should be formulated as ammonia hydrate, $NH_3 \cdot H_2O$.

Ammonium iodide: NH_4I, colorless, hygroscopic, cubic crystals, M_r 144.94, density 2.514, subl.p. 551 °C. The salt is obtained by neutralization of hydroiodic acid with ammonia; it is used in medicine as an expectorant.

Ammoniumiron alum: same as ammoniumiron(III) sulfate.

Ammoniumiron(II) sulfate, ***Mohr's salt***: $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, light green, water-soluble monoclinic crystals; M_r 392.14, density 1.864, dec. 100 to 110 °C. The double salt is less sensitive to oxidation than iron(II) sulfate, and is therefore easier to purify. For this reason, it is used to calibrate $KMnO_4$ standard solutions.

Ammoniumiron(III) sulfate, ***ammoniumiron alum***: $NH_4Fe(SO_4)_2 \cdot 12H_2O$, pale violet, water-soluble, cubic crystals, M_r 482.19, density 1.71, m.p. 39 to 41 °C, conversion at 230 °C to the anhydrous form. A. is used as a mordant in dyeing and printing of textiles and as an astringent in medicine. It is used in quantitative analysis as an indicator in Volhard's titration.

Ammonium nitrate: NH_4NO_3, colorless, hygroscopic monoclinic crystals, rhombic at room temperatures below 32.1 °C; M_r 80.04, density 1.725, m.p. 169.6 °C. Above 200 °C, A. decomposes into dinitrogen oxide and water: $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$. When suddenly heated or ignited, this process occurs explosively. A. dissolves in water with strong cooling. It is made by neutralization of nitric acid with ammonia. A. is an ideal nitrogen fertilizer, because it contains no ballast, but because of the danger of explosion and its hygroscopic properties, it is usually applied in mixtures with other substances. It is a component of safety explosives and the starting material for production of nitrous oxide for medicinal purposes.

Ammonium nitrate gels: gelatinous explosives consisting of nitroglycerin gelatinized with a mixture of collodium wool and nitrotoluene. A. are used to blast hard rocks, even under water.

Ammonium nitrate explosives: often called ***PAC, ANC*** or ***ANFO explosives***: a group of important industrial explosives which contain ammonium nitrate as the main component, a carbon carrier such as coal, oil or sawdust, and sometimes aluminum powder. A. which contain water are important as Slurry blasting agents (see). A. which contain 20 to 40% gelatinized nitroglycerin in addition to ammonium nitrate are called ***gelatin donarites***; they are used in hard rock. ***Donarites*** are A. containing 70 to 80% ammonium nitrate, 4 to 6% nitroglycerin, trinitrotoluene, sawdust, etc. A. which contain no nitroglycerin are called ***ammonites***; examples are powdered mixtures of 80 to 82% ammonium nitrate and 18 to 20% trinitrotoluene. AN-D explosives (see) are ammonites.

Ammonium nitrite: NH_4NO_2, colorless crystalline solid, readily soluble in water; M_r 64.04, density 1.69. In aqueous solution, A. decomposes into nitrogen and water when heated: $NH_4NO_2 \rightarrow N_2 + 2\ H_2O$. The solid explodes at 60 to 70 °C. As a product of various oxidation processes, A. is present in small amounts in the air and in rainwater. It is made by absorption of equal parts of nitrogen monoxide and dioxide in aqueous ammonia; it is occasionally used in the laboratory to produce pure nitrogen.

Ammonium oxalate: $(NH_4)_2C_2O_4 \cdot H_2O$, colorless rhombic crystals, soluble in water and ethanol; M_r 142.11, density 1.50. A. is made by neutralization of oxalic acid with ammonia solution, and is used mainly in analytical chemistry.

Ammonium oxalatoferrate(III), ***iron(III) ammoniumoxalate***: $(NH_4)_3[Fe(C_2O_4)_3] \cdot 3H_2O$, bright green crystals obtained by reaction of iron(III) chloride solutions with ammonium oxalate. Light causes A. to decompose to carbon dioxide and iron(II) compounds. This reaction can be used to measure light and also for photosensitive papers.

Ammonium peroxodisulfate, ***ammonium persulfate***: $(NH_4)_2 \cdot S_2O_8$, colorless monoclinic crystals, readily soluble in water; M_r 228.18, density 1.982. Dry, pure A. is stable up to about 120 °C, but when moist it decomposes rapidly, forming ozone-containing oxygen: $(NH_4)_2S_2O_8 + H_2O \rightarrow 2\ (NH_4)HSO_4 + 1/2\ O_2$. The aqueous solution is strongly oxidizing. A. is obtained by anodic oxidation of ammonium sulfate solution which contains sulfuric acid. It was formerly used mainly to produce hydrogen peroxide. Now it is used as an initiator in polymerization reactions, as a

bleach, deodorant and disinfectant, and in photography and galvanization.

Ammonium persulfate: same as Ammonium peroxodisulfate.

Ammonium phosphates: ***Ammonium dihydrogenphosphate, primary ammonium phosphate***: $NH_4H_2PO_4$, colorless, water-soluble, tetragonal crystals; M_r 115.03, density 1.803, m.p. 190 °C, decomposition above 200 °C with release of ammonia and water. The salt is obtained by neutralization of phosphoric acid with ammonia to a pH of 4. If more ammonia is added, ***diammonium hydrogenphosphate, secondary ammonium phosphate***, $(NH_4)_2HPO_4$, is obtained. This compound forms colorless, water-soluble monoclinic prisms; M_r 132.05, density 1.619. $(NH_4)_2HPO_4$ is a valuable, ballast-free component of multiple-nutrient fertilizers, and is also used as a flame retardant for wood, paper, etc. ***Triammonium phosphate, tertiary ammonium phosphate***, $(NH_4)_4PO_4 \cdot 3H_2O$, is obtained from the reaction of gaseous ammonia with $(NH_4)_2HPO_4$. It forms colorless, water-soluble prisms, M_r 203.13. It is unstable in the solid form, releases ammonia even at room temperature, and, like the other A., decomposes on stronger heating into ammonia and polyphosphoric acid.

Ammonium phthalate: see Phthalamic acid.

Ammonium picrate: $NH_4O\text{-}C_6H_2(NO_2)_3$, the ammonium salt of picric acid, a crystalline compound with a bitter taste, which exists in a yellow and a red modification; m.p. 257 to 259 °C (dec.). A. is soluble in water and ethanol. It is made from ammonia and picric acid, and is a highly brisant explosive. The rate of detonation is 6950 s m^{-1}, which gives A. an explosiveness equivalent to that of 2,4,6-trinitrotoluene (TNT). Its disadvantages, however, are that the melting point is so high and that it cannot be poured into cartridges in molten state.

Ammonium rhodanide: same as Ammonium thiocyanate (see).

Ammonium sodium hydrogenphosphate, *phosphor salt*: $NH_4NaHPO_4 \cdot 4H_2O$, colorless, water-soluble, monoclinic crystals; M_r 209.07, density 1.574. When heated, A. decomposes, forming sodium polyphosphate: $NH_4NaHPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$. It is used in qualitative analysis to make Microcosmic salt beads (see).

Ammonium sulfate: $(NH_4)_2SO_4$, colorless, rhombic crystals, soluble in water with strong cooling; M_r 132.14, density 1.769. Above 235 °C it releases ammonia and is converted to ammonium hydrogensulfate. A. is made on laboratory scale by neutralization of sulfuric acid with ammonia. Industrially, carbon dioxide and ammonia are passed through an aqueous suspension of finely ground gypsum. The calcium carbonate precipitates, and A. is obtained by evaporation of the solution: $2\ NH_3 + CO_2 + CaSO_4 + H_2O \rightarrow CaCO_3 + (NH_4)_2SO_4$. A. was for a long time the most important ammonia fertilizer, but because of its relatively low nitrogen content and acidity, it has been replaced by ammonium nitrate and urea.

Ammonium sulfide: see Ammonium hydrogensulfide.

Ammonium sulfide group: see Analysis.

Ammonium thiocyanate, ***ammonium rhodanide***: NH_4SCN, colorless, deliquescent, monoclinic crystals, readily soluble in water and ethanol; M_r 76.12, density 1.305, m.p. 149.6 °C. At 170 °C, A. decomposes with partial formation of thiourea: $NH_4SCN \rightarrow H_2C(S)NH_2$. It is obtained by the reaction of ammonia with carbon disulfide under pressure. A. is used in analytical chemistry to detect iron(III) ions and in halide determination according to Volhard.

Ammonolysis: see Aminolysis.

AMO explosive: an explosive made of ammonium nitrate and hydrocarbons, such as diesel fuel. A. do not detonate easily and usually require an initial charge. For this reason they are preferred as safety explosives in mining; examples are Dekamon I (94% ammonium nitrate and 6% diesel fuel) or Alumon (addition of sawdust or aluminum powder).

Amonton's law: see State, equation of 1.1.

Amorphous (from the Greek "amorphos" = "without shape"): a term applied to solids in which the constituent particles (atoms, ions or molecules) do not display periodic long-range order. In A. substances, the particles are not completely randomly distributed, however. There is a certain regularity in their arrangement with respect to distance and orientation of nearest neighbors (short-range order). Thus A. substances correspond in their structure to liquids, but differ from them because the particles are not mobile. They are sometimes called *supercooled liquids* in which the friction between particles is very great. All A. have a tendency to convert to the crystalline state, but the process can occur extremely slowly. It can be considerably accelerated by heating.

Solid A. substances are isotropic (crystals are anisotropic). They have no defined melting point, but are converted to the liquid state by a process of slow softening. They can be distinguished from crystalline solids by x-ray diffraction because they do not give sharp interferences; instead they show only a very few diffuse interferences at small diffraction angles. Substances which give this type of x-ray diffraction diagrams are called ***x-ray amorphous***. Only a few naturally occurring substances are x-ray amorphous.

There are many methods of producing the A. state, but only a few of them are universally applicable. Most are limited to a few substances. The most important methods are evaporation and condensation onto a very cold surface (used mainly to produce thin A.layers), very rapid cooling of a melt below its freezing point (used especially for silicate, borate and phosphate glasses and A. semiconductors), precipitation from solutions, application of great mechanical stress to crystalline solids by grinding or polishing, and irradiation with high-energy particles such as ions or neutrons.

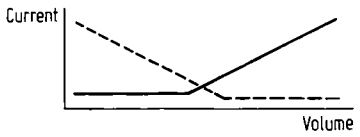
Glasses are among the most important A. Occasionally gases and liquids are called A. due to their lack of long-range order.

Amoxicillin: see Penicillins.

AMP: see Adenosine phosphates.

Amperometry: a method of electrochemical analysis based on the concentration dependence of the diffusion current. An electrochemical cell is used with a reference electrode with a constant electrode potential, an indicator electrode (dropping mercury or platinum electrode) and a suitable electrolyte. A sufficient voltage is applied to cause an electrochemical reaction of the substance to be determined at the

reference electrode. The current flowing in the cell as a result of this reaction is proportional to the concentration of the reacting substance. A well known example of an amperometric determination is the oxygen determination with the Clark electrode. The principle of A. can also be used as a method for recognition of the endpoint of a titration (***amperometric titration***). In the course of the titration, the diffusion current of the substrate drops, reaching the level of the constant base current at the equivalence point. If the titrator rather than the titrand is electrochemically active, an inverted curve is obtained (Fig.).



Signal curves of an amperometric titration. *dashed curve*: titrand electrochemically active; *black curve*: titrator electrochemically active.

Both in A. and in amperometric titration, a second indicator electrode can be used instead of the reference electrode. For A. with two indicator electrodes, the term ***biamperometry*** was formerly used.

"Dead stop" methods are those in which an amperometric titration is carried out with two polarizable electrodes, usually platinum electrodes. The endpoint of the titration is indicated by a sudden flow of current, or by cessation of current ("dead point"). The titrations are usually done at voltages of about 10 mV, and a titration curve is not recorded. The method requires only small amounts of equipment and is used mainly to determine small concentrations of substance.

Amphetamine: C_6H_5-CH_2-$CH(CH_3)$-NH_2, a phenylethylamine derivative which acts as a stimulant; it is addictive. The (S)-configured (+)-enantiomer is called ***dexamphetamine***. A. is the racemate.

Amphibian toxins: toxins sequestered in skin glands of various species of amphibians. Most are mixtures of simple biogenic amines, peptides, steroids and alkaloids. They affect the heart, muscles and nerves. An example of a central effect is the hallucinogenic activity of o-methylbufotenin from the Arizona toad *Bufo alvarius*. Some important A. are batrachatoxin from the Columbian arrow frog, *Phyllobaktes aurotaenia*, with a LD_{50} (mouse) of 2 μg kg^{-1}, and tarichatoxin, which is identical to Tetrodotoxin (see) from pufferfish. Tarichatoxin is present in the Californian salamander *Taricha torosa*, and its LD_{50} (mouse) is 8 μg kg^{-1}. Other A. are samandarin from the European fire salamander, *Salamandra salamandra*, with a LD_{50} (mouse) of 300 μg kg^{-1}, and bufotenin from the toad *Bufo bufo*, with a LD_{50} (mouse) of 400 μg kg^{-1}.

Amphiphilic: adjective describing a compound with both hydrophobic and hydrophilic behavior; surfactants are examples of A. substances.

Ampholyte: a term coined by Brönsted for a substance which acts as both an acid and a base, i.e. one which can either accept or donate a proton. Some typical ampholytes are:

Base effect		Ampholyte		Acid effect	
H_2SO_4	$+ OH^- \rightleftharpoons$	HSO_4^-	$+ H_2O \rightleftharpoons$	SO_4^{2-}	$+ H_3O^+$
H_2CO_3	$+ OH^- \rightleftharpoons$	HCO_3^-	$+ H_2O \rightleftharpoons$	CO_3^{2-}	$+ H_3O^+$
NH_4^+	$+ OH^- \rightleftharpoons$	NH_3	$+ H_2O \rightleftharpoons$	NH_2^-	$+ H_3O^+$
H_3O^+	$+ OH^- \rightleftharpoons$	H_2O	$+ H_2O \rightleftharpoons$	OH^-	$+ H_3O^+$

The amphoteric behavior of water is extremely important for the definition of acid and base strength (see Acid-base concepts, definition of Brønsted acids) and in connection with phenomena related to the Ion product (see) of water.

Amphotenside: amphoteric tensides (surfactants); see Surfactants.

Amphoteric: reacting with both sides. Substances which can act as both acids and bases in the Brønsted sense are A. (see Ampholytes).

Amphotericin B: a polyene antibiotic used as an antimycotic.

Ampicillin: see Penicillins.

AMS: see Herbicides.

Amygdalin: D(-)-mandelic nitrile-β-D-gentiobioside, a cyanogenic glycoside. A. is found in the seeds and leaves of members of the *Rosaceae* family. For example, bitter almonds contain 3 to 5%. A. is cleaved by emulsin, a mixture of enzymes, into glucose, benzaldehyde and hydrogen cyanide.

Amyl acetate: CH_3-CO-OC_5H_{11}, a colorless mixture of isomers with an odor like bananas or pears. The technical product has a boiling range of about 105-148 °C. A. is slightly soluble in water, but dissolves readily in most organic solvents. It is synthesized by esterification of the mixture of isomeric amyl alcohols with glacial acetic acid in the presence of sulfuric acid. A. is used mainly as a solvent for cellulose nitrate, alkyde resins, chlorinated latex, polyvinyl acetate, polystyrene, fats and oils, and as a flavoring and perfume.

Amyl alcohols, ***pentanols***: monovalent alcohols with the general formula $C_5H_{11}OH$; there are eight structural isomers (Table). Except for 2,2-dimethylpropan-1-ol, which is a solid, the A. are colorless liquids with a characteristic odor. They are only slightly soluble in water, but are largely miscible with alcohol and ether.

> Amyl alcohols are injurious to the human organism. Inhaled vapors irritate the mucous membranes, and in higher concentrations act as anaesthetics. The consumption of 12.5 g amyl alcohol has approximately the same toxic effects as 100 g ethanol. Some isomers are highly irritating to the skin; an effect which can be perceived even at 10^4-fold dilution.

For the above reasons, liquors are not allowed to contain more than 0.1% fusel oils. Fusel oils contain 60 to 80% A., and were formerly the most important starting material for production of A. Today they are synthesized mainly by chlorination of pentanes, followed by hydrolysis of the amyl chlorides. As an alternative, the pentene-containing C_5 fractions formed as industrial byproducts can be used; water is added in the presence of sulfuric acid. A. are used widely as

(Amyl alcohols)
Physical properties of the isomeric amyl alcohols

Name	Formula	m.p. [°C]	b.p. [°C]	n_D^{20}
Pentan-1-ol (amyl alcohol)	CH_3-CH_2-CH_2-CH_2-CH_2OH	−79	137.3	1.4101
Pentan-2-ol* (*sec*-amyl alcohol)	CH_3-CH_2-CH_2-$CHOH$-CH_3	–	119	1.4053
Pentan-3-ol	CH_3-CH_2-$CHOH$-CH_2-CH_3	–	115.5	1.4087
2-Methylbutan-1-ol*	CH_3-CH_2-$CH(CH_3)$-CH_2OH	–	129	1.4098
3-Methylbutan-1-ol (*iso*-amyl alcohol)	CH_3-$CH(CH_3)$-CH_2-CH_2OH	–	131	1.4053
2-Methylbutan-2-ol (*tert*-amyl alcohol)	CH_3-CH_2-$C(OH)(CH_3)2$	–	102	1.4052
3-Methylbutan-2-ol*	CH_3-$CH(CH_3)$-$CHOH$-CH_3	–	112	1.3973
2,2-Dimethylpropan-1-ol	$(CH_3)_3C$-CH_2OH 52-53	52−53	113	

* Compounds with asymmetric carbon atoms.

solvents and to make esters. Amyl acetate (see) is particularly important. Pentan-3-ol is also used as a flotation agent in ore processing and as an intermediate for organic syntheses, for example, for production of diethyl ketone by dehydrogenation.

Amylases: enzymes which catalyse the cleavage of 1,4-glycosidic bonds in polysaccharides such as starch, glycogen and dextrins.

α-***Amylases*** are found in saliva, pancreatic secretion and plants, but are now produced industrially using microorganisms. They break down amylose and amylopectin into smaller components (liquification of starch), producing small amounts of maltose and glucose, but mainly the limit dextrins of higher molecular weight. α-A. attack the interior of the starch molecule. Microbial A. are metalloproteins and are stabilized by calcium ions. The pH optimum is 6.5 to 7; the α-A. from *Bacillus licheniformis* is catalytically active up to 110 °C, and is thus one of the most thermostable enzymes.

β-***Amylases*** have so far been found only in plant seeds, where they are active in the breakdown of storage carbohydrates. They are exoenzymes, attacking the molecules from the ends of the chains. They break every second 1,4-glycoside bond, releasing maltose.

Glucoamylase is an exoenzyme which degrades starches and dextrins from the non-reducing chain ends, releasing glucose. The enzyme is formed extracellularly by lower fungi, and is produced on large scale, mainly from *Aspergillus* species (300 t/year). Glucoamylase is thermostable up to 60 °C, and is used in combination with α-A. to make starch hydrolysates containing 94 to 96% glucose.

In the liquor industry, bacterial A. are increasingly replacing the plant enzymes present in sprouting grain (malt).

Amyl chlorides, ***monochloropentanes***: the eight isomeric monochloro derivatives of pentane. ***Amyl chloride (1-chloropentane)***, CH_3-$(CH_2)_4$-Cl, m.p. -99 °C, b.p. 107.8 °C, n_D^{20} 1.4127; ***2-chloropentane***, CH_3-$CHCl$-CH_2-CH_2-CH_3, as the racemate, m.p. -137 to -139 °C, b.p. 96.9 °C, n_D^{20} 1.4069; ***3-chloropentane***, CH_3-CH_2-$CHCl$-CH_2-CH_3, m.p. -105 °C, b.p. 97.8 °C, n_D^{20} 1.4082; ***1-chloro-2-methylbutane***, CH_3-CH_2-$CH(CH_3)$-CH_2-Cl, as the racemate, b.p. 99.9 °C, n_D^{20} 1.4102; ***isoamyl chloride (1-chloro-3-methylbutane)***, CH_3-$CH(CH_3)$-CH_2-CH_2-Cl, m.p. -104.4 °C, b.p. 98.5 °C, n_D^{20} 1.4084; ***tert-amylchloride (2-chloro-2-methylbutane)***, CH_3-$CCl(CH_3)$-CH_2-CH_3, m.p. -73.5 °C, b.p. 85.6 °C, n_D^{20} 1.4055; ***sec-isoamylchloride (2-chloro-3-methylbutane)***, CH_3-$CHCl$-$CH(CH_3)$-CH_3, as the racemic form, b.p. 92.8 °C, n_D^{20} 1.4020; ***neopentylchloride (1-chloro-2,2-dimethylpropane)***, m.p. -20 °C, b.p. 84.3 °C, n_D^{20} 1.4044.

A. are colorless liquids which are only slightly soluble in water, but dissolve readily in many organic solvents. They are synthesized by thermal chlorination of pentane-isopentane mixtures. The reaction mixture contains all isomeric A. except neopentyl chloride. This can be produced by chlorination of neopentane at 0 °C. A. are used to produce amyl alcohols, amyl amines, amyl mercaptans and aromatic amyl derivatives.

Amylenes: same as Pentenes (see).

Amylopectin: see Starch.

Amylose: see Starch.

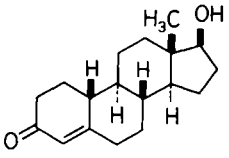
Amylum: same as Starch (see).

Amyran: see Triterpenes.

Amyrin: see Triterpenes.

An: a frequently used general symbol for actinides.

Anabolics, ***anabolic steroids***: a group of synthetic steroids which have anabolic effects: they promote protein biosynthesis and retention of nitrogen in the body. This leads to an increase of muscle mass. In 1935, the anabolic effect of testosterone was discovered. In order to separate the androgenic and anabolic effects of the hormone, so that the anabolic effect could be utilized in therapy of women and children, partially and totally synthetic steroids were developed. Some examples of A. are *nandrolone* (Fig.) and its esters, such as the decanoate; others are *methenolone acetate (Primobolane®)* and *stanozolol (Stromba®)*.



Nandrolone

Anabolic steroids: same as Anabolics (see).

Analeptics: compounds which enhance the excitability of the central nervous system. In therapeutic doses, they act as stimulants, especially of the respiratory and vasomotor centers. In higher doses, they

cause cramps, which can be relieved by barbitals. Natural products such as strychnine, picrotoxin, camphor and lobelin have analeptic effects. They are now rarely used for this purpose, however. Caffeine has a weak analeptic effect. Today the most commonly used A. are synthetic compounds such as pentetrazol and bemegrid, and various *N,N*-dialkylsubstituted aromatic or heteroaromatic carboxylic acid amides. Phenylethylamine derivatives which stimulate the central nervous system, and thus counteract the need for sleep, are sometimes considered A. These compounds temporarily increase physical and mental capacities, and in some persons cause euphoria. They have only slight effects on the heart activity and blood pressure. A side effect is depression of the appetite, which has been utilized in Appetite suppressants (see). The best known phenylethylamines of this type are Amphetamine (see) and Methamphetamine (see).

Analgesics: compounds which, in therapeutic doses, are able to relieve pain through their effects on centers in the cerebral cortex. The do not affect the other functions of the central nervous system, and do not cause loss of consciousness. Strong A. are also called *narcoanalgesics*; weaker A. cannot suppress severe pain, but often also act as Antipyretics (see) and Antiphlogistics (see).

The strong A. include morphine and structurally similar compounds, pethidine and methadone. The weak A. include derivatives of salicylic acid, such as acetylsalicylic acid and salicylamide, pyrazolones such as phenazone, aminophenazone, analgin and propyphenazone, and aniline derivatives, such as phenacetin and paracetamol.

Various A. are combined with other drugs, such as barbitals, and are very widely used.

Analgin: see Pyrazolones.

Analysis: the determination of the composition of a substance or mixture of substances. The process is subdivided into qualitative, quantitative and structural A.

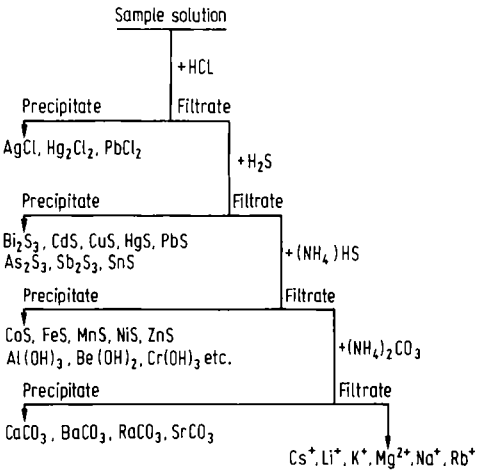
Qualitative A. is the determination of the nature of the components of a substance. In inorganic chemistry, qualitative A. is essentially elemental analysis, but in organic chemistry, where the elemental compositions of the molecules are very similar, a different type of information is also sought. Both chemical and physical methods are used. This section treats mainly the chemical methods, because the physical methods can also be used for quantitative and structural analysis, and are discussed in those sections.

Preliminary tests are used to determine whether certain substances are present, and/or to obtain information on the composition and chemical behavior of the sample. They are used to indicate the best strategy for the subsequent A., and thus precede but do not take the place of separation into groups. General information on the behavior of the sample is provided by solubility experiments, dry heating in closed tubes, Blowpipe analysis (see) and Microcosmic salt beads (see). There are also special tests used for certain elements or substances. Such tests are used especially to detect strong poisons, for example, the Berzelius test (see), the Bettendorf test (see), the Gutzeit test (see) and the Marsh test (see) indicate the presence of arsenic. In organic qualitative A., certain tests (see Beilstein test, Hepar test and Lassaigne test) indicate the presence of certain elements.

After the preliminary tests, solid samples are dissolved, which homogenizes them. If this is not possible, or if a solid residue remains, Solubilization (see) is required. The components of the resulting sample solution are then identified by adding reagents which cause them to precipitate or change color. The sensitivity of such reactions can be characterized by the Limit concentration (see) and the Limit of detection (see). Identification of a component is only positive if the reagent is specific for that component alone. However, most reagents are not selective for a single substance, but rather react with a number of substances, so the identification is not unique.

A systematic *separation process* is used to separate the components of a sample into groups. Usually this is done by adding "group reagents" in a sequence which separates possible components into groups by precipitation. Within each group, a positive identification of the components can be made with nonspecific reagents or reactions. Different separation processes are known for cations, anions and organic compounds. In the Fresenius system for cations (Table 1), the *hydrochloric acid group*, silver, mercury(I) and lead ions, is precipitated as chlorides, and thus separated from the other cations.

Table 1. The Fresenuis separation system for cations.



The *hydrogen sulfide group*, consisting of arsenic, antimony, lead, cadmium, copper, mercury(II), bismuth and tin ions, is separated as the insoluble sulfides. The *ammonium sulfide group* consists of iron, cobalt, nickel, manganese, indium, thallium and zinc ions, which are precipitated as their sulfides, and aluminum, beryllium, chromium, hafnium, lanthanum, niobium, tantalum, titanium, thorium, scandium, uranium, yttrium and zirconium ions, which are precipitated as hydroxides or oxide hydrates. The *ammonium carbonate group* consists of calcium, barium, radium and strontium ions, which precipitate as carbonates.

In this way it is possible to determine the qualita-

tive composition of all inorganic substances using chemical methods. Methods of Microanalysis (see) are available for use with very small amounts of sample; Drop analysis (see) is a special type of microanalysis.

In qualitative organic A., the elements can be identified with simple preliminary tests, but it is difficult or imposible to identify definite compounds by chemical methods alone. Therefore, the first step is to identify the functional groups which are present, e.g. carboxyl, carbonyl, hydroxyl, amino, nitro, mercapto and sulfonic acid groups, using chemical methods. It is often necessary to carry out separations, such as distillation, extraction, crystallization, or especially chromatography, before identification is possible. The isolated compounds are then often identified by characteristic constants or by means of other physical methods. In all qualitative A., the course of the identification reaction or the intensity of the signal from a physical method gives an indication of the amount of the component present.

Quantitative A. is used to determine the amounts of the components of a substance. It requires knowledge of the qualitative composition of the sample. In many cases, the results of quantitative A. are economically important, as in the determination of metal contents of ores, control of the compositions of alloys, or quality control of chemical processes. In such cases, the sample is taken from a very large amount of material, and accurate Sampling (see) techniques are required. There are many different physical and chemical methods for quantitative A. Chemical methods require relatively little apparatus and do not need to be calibrated, because they are based on the laws of Stoichiometry (see). Their disadvantage is the amount of time they require, which is often considerable, and their unsuitability for series A. They are also of little use for continuous determinations for controlling and directing industrial processes.

For quantitative A., as for qualitative A., solid samples must first be dissolved using chemical methods. Before the actual determination, the component to be determined must often be separated from interfering substances which may be present. This can be done by extraction or chromatography. In some cases, such separations can be avoided by use of Masking reagents (see).

The chemical methods of quantitative A. can be classified as 1) Gravimetric A. (see), 2) Volumetric A. (see), electrochemical A., such as Amperometry (see), Coulometry (see), Conductivity measurements (see), Polarography (see) and Potentiometry (see), 4) optical methods such as Colorimetry (see), Nephelometry (see) and Photometry (see).

In contrast to chemical methods, the physical methods of quantitative A. are relative rather than absolute, and must therefore be calibrated. The composition of the calibration reagents must be determined by very precise chemical methods. The advantage of physical methods is that they can be done rapidly and are especially suitable for series analyses; the sample preparation is also often simpler. The disadvantage is that the equipment is often very expensive. These methods can be classified on the basis of the underlying physical processes, for example, 1) atomic spectroscopy (see Atomic emission spectroscopy, Atomic absorption spectroscopy and Atomic fluorescence spectroscopy) 2) x-ray spectroscopy (see X-ray fluorescence analysis), 3) radiochemical methods (see Activation analysis) and 4) Mass spectroscopy (see).

The methods used for structural A. can also be used in special cases for quantitative A.

The results of a quantitative A. are usually given in mass % of the components. If all the components of a substance are determined, one speaks of ***complete A.***

The methods of A. can be classified according to the amounts of sample used: ***macroanalyses*** require about 1 g sample, while ***microanalyses*** require only μg to mg of sample. Further subdivisions are ordinarily indicated by use of the prefixes "semi-", "ultra-" and "sub-".

Another classification can be based on the amounts of the components. Major component A. is concerned with the components which make up 10 to 100% by mass, minor component A. deals with the range of 1% to 10%, and Trace analysis (see) applies to the range below 1%. Traditionally, the methods of A. are also classified according to the nature of the substance under study, for example, Elemental A. (see), 2) Gas A. (see), 3) Clinical A. (see), 4) Metal A. (see), 5) Silicate A. (see) and Water A. (see).

The capacities of the various methods cannot be generalized. For example, the values for reproducibility and accuracy of an analytical method which are determined by statistical methods depend also on the nature and composition of the sample. On the other hand, the limits of detection of the various methods can be relatively accurately indicated (Table 2).

Table 2. Comparison of the limits of detection of a few selected analytical methods with those of natural sense organs

Method	Limit of detection in g
Chemical methods	to 10^{-9} g
Electrochemical methods	10^{-12}
Atom emission spectrometry	10^{-12}
Mass spectroscopy	10^{-13}
Human nose	10^{-13}
Activation analysis	10^{-14}
Electron microprobe	10^{-16}
Canine nose	10^{-18}
Bee sense of smell	10^{-20}

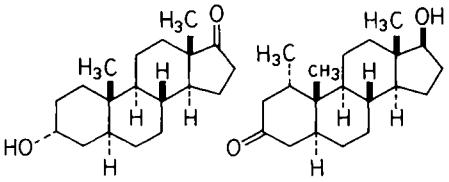
Structural A. is concerned with elucidation of the structure of a compound, and is of great importance in organic chemistry, but is also applied in inorganic chemistry, especially in complex chemistry. The sample must be a pure substance, not a mixture. The main methods of structural A. are those of molecular spectroscopy, e.g. Infrared spectroscopy (see), UV-VIS spectroscopy (see) and NMR spectroscopy (see), combined with Mass spectroscopy (see). These methods do not give direct information on the structure of a compound, but only indicate the ranges in which a molecule can absorb energy. The connection between the structure of the molecule and the signal of the method can only be interpreted on the basis of empirical comparisons. A combination of the results of different methods often provides a clear indication of the structure of the compound. However, it is not possible in this way to obtain information on the bond lengths and angles in large molecules. A complete

structural elucidation of very complicated compounds is only possible with diffraction methods, such as x-ray and electron diffraction (see X-ray structure analysis). These methods can be used only with solids in the form of single crystals (to some extent, also with powders), and require extensive calculations, so they have only become widely applicable since the introduction of modern data analysis systems. The result is a complete picture of the structure of the compound studied, which, however, is exact only for its crystalline state.

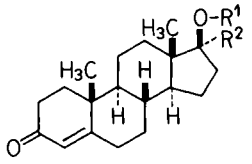
Analytical chemistry: see Chemistry.

AN-D explosives: abb. for ammonium nitrate-diesel explosives used in industry. They consist of 92.5 to 96% fine-grained, free-flowing ammonium nitrate, NH_4NO_3 and 4 to 7.5% diesel fuel. Because they are not very sensitive to mechanical effects (they require a special ignition cap for detonation), these are relatively safe explosives. In some countries, they are mixed at the site of use, and then poured or blown into the boreholes with compressed air.

Androgens: a group of steroids which act as male sex hormones. The natural A. are derivatives of ***androstane***; they thus contain 19 C atoms and have oxygen functions on C atoms 3 and 17. The main natural A. is ***testosterone***, 17β-hydroxyandrost-4-ene-3-one. Other derivatives of androstane, such as the testosterone metabolite ***androsterone***, have an androgenic effect, although it is much weaker. Testosterone is synthesized in the interstitial cells of the testes, the *Leydig cells*, in response to gonadotropic hormone (see Gonadotropins). 17α-Hydroxyprogesterone is converted to 4-androstene-3,17-dione by removal of the C_2 chain on C-17; this is then reduced to testosterone, a white crystalline solid with m.p. 155 °C, $[\alpha]_D^{20}$ + 109° (ethanol).



Androsterone Mesterolone



Name	R^1	R^2
Testosterone	H	H
Testosterone propionate	CH_3-CH_2-CO-	H
Testosterone enanthate	$CH_3-(CH_2)_5-CO-$	H
Methyl testosterone	H	CH_3

Testosterone is soluble in acetone, ethanol and chloroform. It is partially synthesized from androstenolone (5-androsten-3-ol-17-one), or is produced microbiologically from progesterone. The sexually specific effects of testosterone include induction of secondary male sexual characteristics and maintenance of accessory gland function in the genital tract, spermogenesis and libido. In addition, it has sexually unspecific, anabolic effects (see Anabolics). Testosterone is injected in patients who do not produce enough androgens; orally applied testosterone is too rapidly metabilized to be useful. Esters, such as testosterone propionate, are effective for longer periods and are used for that reason. Esters with longer-chain fatty acids, such as the enanthate (heptoate), have depot effects. ***Methyl testosterone***, with a 17α-methyl group, and ***mesterolone***, with a 1α-methyl group, are effective upon oral administration. The 17α-methyl group inhibits dehydrogenation to the 17-keto compound, and the 1α-group prevents binding to metabolizing enzymes.

Historical: The first A. isolated was androsterone, which was extracted from human urine in 1931 by Butenandt and Tscherning. Testosterone was isolated from bovine testes in 1935 by Laqueur. Its structure was determined and partial synthesis reported in the same year; the principal investigators were Butenandt and Ružcvka. Total synthesis was achieved in 1955 by Johnson.

Androstane: see Androgens.

Androsterone: see Androgens.

Andrusov process: see Natural gas.

Anergy: see Exergy.

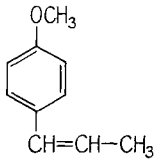
Anesthesin®: see Anesthetics, local.

Anesthetics, local: compounds which reversibly inhibit the excitability and conductivity of nerves in a limited area. The effect depends on an inhibition of the flow of sodium ions into the nerve cells. A. are used for surface or mucous membrane anesthesia, in which primarily the nerve endings are affected, for conduction anesthesia, in which the transmission of impulses in a nerve trunk is interrupted, and for infiltration anesthesia, in which the nerve endings and smaller nerve fibers in the infiltration area are affected.

A. which are relatively stable to metabolism are also used in cases of cardiac arhythmia. The first A. was the alkaloid Cocaine (see), which was used in opthamology in 1884. Synthetic compounds replaced natural alkaloids many years ago. The first of these was ***benzocaine*** (***Anesthesin®***), 4-$(H_2N)C_6H_4COOC_2H_5$, the ethyl ester of 4-aminobenzoic acid. Because of the low basicity of the amino group, solutions of the hydrochloride are acidic and are not suitable for injection. The next development was of basic esters of 4-aminobenzoic acid; the first of this group was ***procaine*** (***Novocaine®***), 4-$(H_2N)C_6H_4COOCH_2CH_2N(C_2H_5)_2$, the 2-diethylaminoethanyl ester of 4-aminobenzoic acid. Aqueous solutions of procaine hydrochloride are nearly neutral and are very suitable for injection. Later, variations in the substituents on the benzene ring and in the alcohol component were developed. The most widely used of these compounds is ***tetracaine***, $4(n)C_4H_9$-NH-C_6H_4-$COO(CH_2)_2$-$N(CH_3)_2$, a surface anesthetic. A. with ester structures are rather unstable. Base-substituted carboxyanilides such as ***lidocaine (Xylocitrin®)***, $2,6-(CH_3)_2$-C_6H_3-$NHCOCH_2$-$N(C_2H_5)_2$, are more stable, due to the ortho-substituent and the anilide structure. The surface anesthetic ***propipocaine***

(***Falicaine***®) is an example of a β-aminoketone type A.

Anethol: 4-methoxypropenylbenzene, a phenol ether. The crystals are colorless, pleasant-smelling platelets; m.p. 22-23 °C, b.p. 235 °C, n_D^{20} 1.5615. A. is insoluble in water, soluble in ethanol, ether and other organic solvents. It is synthesized from 4-methoxyphenylmagnesium bromide and allyl bromide. The primary product is estragol (4-methoxyallylbenzene); this isomerizes in the presence of alkali hydroxide to A. Oxidation by nitric or chromic acid forms anisaldehyde. A. is the main component of anis oil, and is also present in tarragon and fennel oil. It can be extracted from anis oil and is used in perfumes and liquors. Because of its mucus-loosening effect, it is also used in cough medications.



Anethol

Aneurin: same as Vitamin B_1 (see).

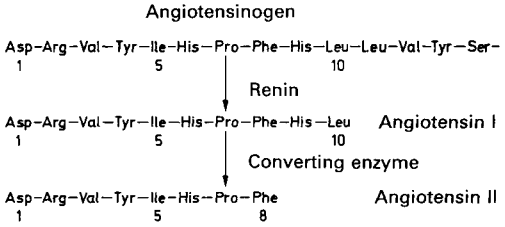
Angelicin: see Furocoumarins, Table.

Angeli-Rimino reaction: a method of synthesizing hydroxamic acids from aldehydes and benzenesulfonylhydroxylamine under alkaline conditions:

$$R\text{–}CHO + C_6H_5\text{–}SO_2\text{–}NH\text{–}OH \xrightarrow{(OH^-)} R\text{–}CO\text{–}NH\text{–}OH + C_6H_5\text{–}SO_2H$$

The A. is also a reductive conversion of the sulfonic acid derivative to a sulfinic acid.

Angiotensin, ***angiotonin, hypertensin***: a peptide tissue hormone. The inactive precursor of A., ***Angiotensin I*** is released from a plasma α_2-globulin (angiotensinogen) by the kidney protease renin. A converting enzyme, a chloride-dependent, EDTA-sensitive dipeptidase, converts A. I to a vasoactive octapeptide, ***angiotensin II***. The [Ile^5]A.II of human beings, pigs and horses has the same biological effects as [Val^5]A.II from cattle.



A. strongly elevates blood pressure and stimulates aldosterone production in the adrenal cortex. It also has an effect on the smooth muscles, which is not thought to have any physiological significance. The first total synthesis was reported in 1957. Many analogs have been prepared; the antagonists are of great interest, as are inhibitors of the converting enzyme, for reducing high blood pressure.

Angiotensinogen: see Angiotensin.

Angiotonin: same as Angiotensin (see).

Anhalonium alkaloids: see Alkaloids, Table.

Anharmonic oscillator: see Infrared spectroscopy.

Anhydrite: anhydrous calcium sulfate; see Gypsum.

Anhydro compound: see Purpurea glycosides.

Anhydrosugars: intramolecular ethers of monosaccharides. The oxygen ring usually contains three or five atoms. The A. are synthesized from halogen compounds, or sulfonate or sulfate esters. A. occur naturally, in the form of 3,6-anhydro-L-galactopyranose residues in various galactans.

Anid®: see Synthetic fibers.

Aniles: see Schiff's bases.

Anilides: N-phenyl-substituted carboxamides with the general formula R-CO-NH-C_6H_5. They can be hydrolysed by bases or mineral acids to aniline and the corresponding acids. A. are formed by reaction of anhydrous carboxylic acids, acyl halides or anhydrides with aniline. For example, acetanilide is formed from acetic anhydride and aniline: $(CH_3\text{-}CO)_2O + NH_2\text{-}C_6H_5 \rightarrow CH_3\text{-}CO\text{-}NH\text{-}C_6H_5 + CH_3\text{-}COOH$. A. are often used to characterize carboxylic acids and in the production of drugs and pesticides.

Aniline, ***aminobenzene, phenylamine***: $C_6H_5\text{-}NH_2$, the simplest aromatic primary amine. A. is a colorless, oily liquid with an unpleasant odor, which quickly turns brown in the air; m.p. - 6.3 °C, b.p. 184 °C, n_D^{20} 1.5863. A. is nearly insoluble in water but dissolves readily in most organic solvents; it can be steam distilled. It can be detected by the Runge lime chloride test; oxidation of A. leads to a characteristic red-violet, quinoid pigment. The free electron pair on the N atom makes A. basic, but resonance interaction of this pair with the ring electrons makes A. less basic than aliphatic primary amines. It forms stable salts with strong acids, for example, Aniline hydrochloride (see) with hydrochloric acid. Acylation of A. produces Anilides (see). Another important reaction of A. is condensation with aldehydes and ketones, forming Schiff's bases. The reaction of A. with nitric acid produces a phenyldiazonium salt which is essential for the production of azo dyes. A. reacts wtih carbon disulfide on heating in alcoholic solution, forming N,N'-diphenylthiourea, from which phenyl isothiocyanate can be formed. Under suitable conditions, A. can be oxidized specifically to phenylhydroxylamine, nitrosobenzene or nitrobenzene. The oxidation of A. to *p*-benzoquinone is important, and its condensation reactions with azobenzene derivatives are of interest for synthesis of symmetric or unsymmetric azobenzene derivatives. Under strongly basic conditions, A. forms the unpleasant-smelling benzoisonitrile (see Isonitrile reaction).

Aniline is a strong blood and nerve poison. It can enter the body through the lungs or skin. Very small amounts can be detoxified in the body by conversion to 4-aminophenol, and excreted in this form. Mild poisoning produces blue coloration of the lips, nose, ears and fingernails (cyanosis), diz-

ziness and excitability. Oral intake leads to vomiting, cramps and diarrhea. In severe poisoning, aniline causes headaches, apathy, faintness, loss of awareness, irritation of the bladder and difficulty in breathing. Chronic symptoms are weakness, loss of appetite, neurasthenic symptoms, skin rashes and bladder growths which can become carcinomas. In the blood, aniline leads to formation of methemoglobin, and thus to loss of oxygen transport.

First aid: bring the patient into fresh air; remove clothing which is soaked in aniline, and wash the affected skin. Spray with cold water, give artificial respiration, preferably with oxygen, and call the doctor!

A. occurs naturally in coal tar. Industrially, it is made in large amounts by the Bechamp method, by reduction of nitrobenzene with iron and hydrochloric acid, or by catalytic hydrogenation of nitrobenzene in the presence of copper catalysts. It is also produced industrially by ammonolysis of chlorobenzene or phenol with suitable catalysts. A. is one of the most important starting materials for industrial synthesis of aromatic products, such as dyes, pharmaceuticals, photographic developers, pesticides, substituted A., A. resins, phenylhydrazine, etc.

Historical. A. was first isolated in 1826 by Unverdorben, by lime distillation of natural indigo. It was later detected in coal tar distillate by Runge (1834); in 1841, Fritsche discovered the same compound in alkali melts of indigo. Finally, it was synthesized in 1842 by Sinin, by reduction of nitrobenzene. In 1843, Hofmann demonstrated the identity of the four isolated substances. After Perkin had made the first synthetic aniline dye, industrial production of A. began in 1857.

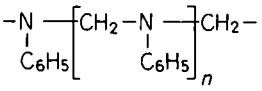
Aniline black: an important black developing dye. A. is almost completely insoluble in water. It is nearly always synthesized directly on the fiber by oxidation of aniline with potassium chlorate (***chlorate black***) or potassium dichromate (***dichromate black***). A complicated series of reactions produces a chain of eight aromatic rings. Some intermediate products are the red and blue ***emeraldine bases***, which are indamines and are converted to light-fast triazine derivatives. A. was discovered in substance by F.F. Runge.

Aniline dyes: see Pigments.

Aniline hydrochloride, ***anilinium chloride***: $C_6H_5NH_3Cl$, the most important salt of aniline. A. forms white crystals with m.p. 198 °C, b.p. 245 °C. It is soluble in hot water and alcohol, and insoluble in ether. In aqueous solution, A. is largely dissociated. It is often used in syntheses instead of aniline, for example in the production of phenylisocyanate from A. and phosgene. A. is produced from aniline and hydrochloric acid, and is used for synthesis of various aniline intermediates and dyes.

Aniline purple: same as Mauveine (see).

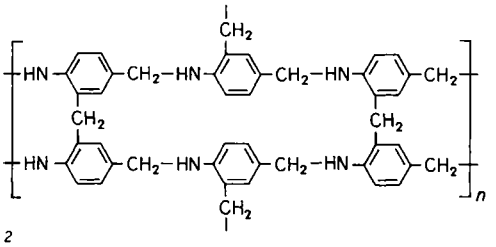
Aniline resin: a hard aminoplastic. There are three types. 1) Non-cross-linked, non-hardening, brittle, colophony-like, soluble and meltable A. are obtained by condensation in neutral or slightly alkaline medium.



1

The starting materials for this type are formaldehyde and, usually, anilines, but toluidines, naphthylamines, diamines and secondary amines (e.g. benzylaniline) are also used. Other aliphatic or aromatic aldehydes can be used instead of formaldehyde. This type of A. is used for paints and textile conditioning.

2) Cross-linked, non-melting A. are made by condensation in highly acidic media. These materials are thermoplastic around 150 °C, but they do not become liquid. The aldehyde component is always formaldehyde, and only primary aromatic amines are used. The primary chains are cross-linked by addition of excess formaldehyde, creating resins which can be used with fillers to make plastics with good mechanical and electrical properties.



2

3) Completely insoluble A. which do not soften when heated are made by condensation of aniline and other amines with furfural.

Aniline yellow: same as 4-Aminoazobenzene (see).

Anilinium chloride: same as aniline hydrochloride.

Anilinoacetic acid: same as *N*-Phenylglycine (see).

Animal pigments: natural pigments from animals; see Pigments.

Animal starch: same as Glycogen (see).

Animal toxins: Poisons (see) regularly formed by many animals under normal living conditions; a high toxicity is necessary. The A. include chemically very diverse substances; most of them are mixtures of different components (e.g. the snake toxins). Their chemical nature has not been thoroughly explored, and the toxic effects cannot be ascribed to chemically defined substances in every case.

Many A. contain proteins of high molecular weight; these are related to the microbial toxins. Many of them have high sulfur contents, which often parallel their toxicity.

Toxic substances of low molecular weight include many which are probably protein degradation products, e.g. methylated amines in the foul-smelling secretions of many beetles and caterpillars; betaines such as stachydrin and trigonellin in sea urchins; adrenalin and tryptamin derivatives (e.g. bufotenin) in various toad poisons.

The effects of the individual A. and their components are various, and the mechanisms are often unknown. The heart is commonly affected (toad poisons), or the blood (e.g. agglutination, coagulation, inhibition of clotting), or central nervous system (e.g. depression of the respiratory center, excitation). The most important of the A. are found under the following separate entries: Ant toxins, Amphibian toxins, Bee toxins, Fish toxins, Insect toxins, Jellyfish toxins, Snake toxins, Scorpion toxins.

Anion: an Ion (see) with one or more negative charges. The term was originally defined by Faraday only in connection with electrolysis: the particles which move toward the anode (the positive electrode) in electrolysis are A.

Anion base: see Acid-base concepts, section on Brønsted definition.

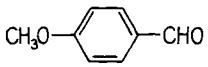
Anion chromatography: see Ion chromatography.

Anion exchanger: see Ion exchanger.

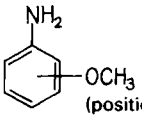
Anionics: non-ionic Surfactants (see).

Anion acid: see Acid-base concepts, section on Brønsted definition.

Anisaldehyde, ***4-methoxybenzaldehyde***: a colorless, pleasant-smelling liquid; m.p. - 0.02 °C, b.p. 248 °C, n_D^{20} 1.5730. A. is slightly soluble in water and infinitely soluble in alcohol and ether. It is steam volatile and can be separated from reaction mixtures and purified by steam distillation. Like most Aldehydes (see), A. is very reactive and undergoes the typical addition and condensation reactions, with the exception of those in which α-H atoms are required. It is readily converted to anisic acid by oxidation in air. A. occurs in nature as a component of anis and fennel oils. It can be synthesized technically from anethol by oxidation with nitric acid, chromic acid or ozone. A. can also be synthesized by methylation of 4-hydroxybenzaldehyde or by a Vilsmeier-Haack reaction (see) from anisol. A. is used mainly as a perfume.



Anisidines, ***aminoanisoles, methoxyanilines, aminophenyl methyl ethers***: the three isomeric methoxy deriviatives of aniline. ***o-Anisidine*** is a yellow, unstable liquid; m.p. 6.2 °C, b.p. 224 °C, n_D^{20} 1.5713. ***m-Anisidine*** is an oily liquid, b.p. 251 °C, n_D^{20} 1.5794. ***p-Anisidine***, crystal platelets (from water); m.p. 57.2 °C, b.p. 115 °C at 1.73 kPa. The A. are slightly soluble in water, but readily soluble in alcohol, acetone, ether and benzene. They are more basic than aniline, due to the electron-shifting effects of the methoxy group. The A. are synthesized by reduction of the corresponding isomeric nitroanisols. They are used in the production of drugs and azo dyes.



(position 2, 3 or 4)

Anisol, ***methoxybenzene, methyl phenyl ether***: C_6H_5-OCH_3, a colorless, combustible liquid with a pleasant odor; m.p. - 37.5 °C, b.p. 155.4 °C, n_D^{20} 1.5179. A. is insoluble in water but readily soluble in ethanol and ether. It is obtained by reaction of phenol with dimethylsulfate in alkali hydroxide solution. It is used as a high-boiling solvent in organic syntheses, e.g. in Grignard reactions.

Anisotropy: a dependence of physical properties and behavior of substances on direction. A. is most common in crystals, but is also found in liquid crystals and, under certain conditions, even in liquids. Polycrystalline substances can be anisotropic if the crystallites are not randomly oriented (see Texture). The A. of a crystal is determined by its lattice structure (geometric A.); it is observed, e.g. in electrical and thermal conductivity, elasticity, hardness, cleavage directions, thermal expansion, rate of crystal growth and optical properties. All crystals are not equally anisotropic; e.g. cubic crystals are optically isotropic, although they are anisotropic in other respects, such as growth rates and cleavage planes. Antonym: Isotropy (see).

Anisic acid, ***4-methoxybenzoic acid***, 4-CH_3O-C_6H_4-COOH, colorless prisms or needles, m.p. 184 °C, b.p. 277 °C. A. is slightly soluble in water, but readily soluble in alcohol, ether and benzene. It dissolves in bases, forming salts. A. is present in anethol-containing essential oils. It can be synthesized by oxidation of anethol with potassium permanganate or by a Grignard reaction (see) from 4-methoxyphenylmagnesium bromide and carbon dioxide.

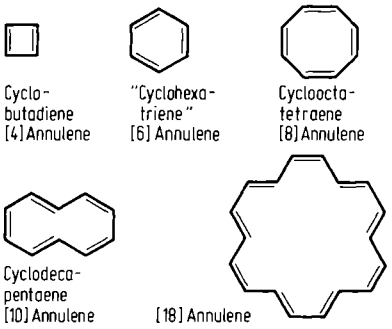
Annealing: treatment of a hardened or cold-worked metal object (usually steel) at a temperature below the first crystal-structure conversion temperature. A. at high enough temperature to improve the mechanical properties is called tempering. During A. thin layers of oxide form on the surface of the metal, and these display interference colors. If objects with clean surfaces are used, these colors permit certain determination of the annealing temperature in the range from 220 to 230 °C.

A. may also be used to dissolve alloy components which precipitate out at low temperatures, or, in a vacuum or under a protective gas, A. can be used to remove an oxide layer.

Annihilation: the interaction between two electronically excited species leading to formation of one species in the ground state and one in an electronically excited state. In triplet-triplet A., both of the interacting species are in excited triplet states; one of the resulting species is in the singlet ground state and the other is in a singlet excited state. The singlet excited species is usually deactivated by a delayed fluorescence.

Annulenes: cyclic, conjugated hydrocarbons with different ring sizes. The A. are named by placing the even number *n* of CH groups in the ring system in square brackets in front of the word "annulene"; *n* = 4, 6, 8, 10, etc.

In addition, the compounds can be given systematic names: cyclobutadiene, cyclooctatetraene, cyclodecapentaene, etc. The "hypothetical" cyclohexatriene does not exist as a cyclic conjugated ring system and is excluded (see Benzene). Cyclobutadiene



(see) and Cyclooctatetraene (see) are also often treated separately. The four- and eight-membered rings and other A. with $4n\pi$ electrons (n = 1, 2, 3, 4...) have higher energies than hydrocarbons with the corresponding numbers of isolated double bonds, and are called "*antiaromatic*". If the cyclic conjugated system contains $4n + 2$ electrons, as benzene does (n = 1), the system has lower energy than comparable systems with isolated double bonds, and it is *aromatic* (Hückel rule). [10]Annulene corresponds to the Hückel rule with respect to its electronic structure. It has 10 π electrons in a cyclic conjugated ring system, but it is not planar and is therefore not resonance stabilized; the two H atoms in positions 1 and 6 prevent flattening. Because of this steric hindrance, it does not generate a diamagnetic ring current in a magnetic field, as would be typical of an aromatic, and it is atropic. [14]Annulene, too, which should be aromatic by the Hückel rule, is not completely planar for steric reasons and does not display a diamagnetic ring current. Only in [18]annulene are all the conditions for an aromatic compound fulfilled. In addition to having $4n + 2$ π electrons (n = 4), it is completely planar and has a diamagnetic ring current. Therefore, in a nuclear magnetic spectrometer, all the peripheral protons give a single signal because all are equivalent (δ = 8.8 ppm). [18]Annulene is diatropic, and it is chemically very stable. It is one of the non-benzoid aromatics.

A. with 12, 16 or 20 ring members are antiaromatic and display the properties of polyenes. [16]Annulene has been particularly thoroughly studied; in it, a paramagnetic ring current is induced by an external magnetic field. This means that the signals from the external ring protons are shifted to higher field, while those from the internal ring protons are shifted to lower field.

Anode: see Electrode.

Anodic corrosion protection: see Electrochemical corrosion protection.

Anodic oxidation: oxidation which occurs at the anode of an electrolysis cell through which current is flowing. A. is the basis of various industrial processes, e.g. electrolytic production of chlorine.

Protective oxide coatings on metals, especially aluminum, magnesium and their alloys, can also be produced by A. In aluminum, A. is also called ***aloxidation*** or ***eloxation*** (***eloxal process***, abb. for electrolytically oxidized aluminum). This process is used to generate a corrosion- and wear-resistant layer, 10 to 30 µm thick, on the surface of aluminum and its alloys. The workpiece is connected to the cell as anode, and dipped in a bath of sulfuric or oxalic acid. The resulting colorless layer can also be dyed with an organic pigment, e.g. for materials used in construction of buildings. The porosity in the layer can be removed by boiling in water or treatment with hot chromate, acetate or silicate solution; this process is called ***sealing***. The layers are electrically insulating.

A special process of A. is ***hard eloxation***, which produces gray to gray-black, hard and abrasion-resistant layers up to about 150 µm thick.

With other metals, A. can be used to a certain extent to produce thin, non-porous oxide layers with special electrical properties, e.g. for electrolyte capacitors and rectifiers. A. is sometimes used to create an oxide layer with better lubricating qualities than the underlying metal, which makes it easier to shape the piece.

Organic substrates can also be subjected to A. (see Organic electrosynthesis). Finally, A. is also used in waste-water treatment.

Anolyte: see Electrolysis.

Anomers: see Stereoisomerism, 1.2.1; see Monosaccharides.

Anorexics: same as Appetite suppressants (see).

Ansa compounds: see Cyclophanes.

Ansamycins: antibiotic ansa compounds produced by microorganisms (*Streptomyces, Nocardia* and *Micromonospora* species). They contain an aromatic nucleus which is bridged by an aliphatic side chain. The A. are classified on the basis of the aromatic nucleus as naphthalene or naphthoquinone derivatives, including the streptovaricins, rifamycins, halomycins, tolypomycins and naphthomycins, and the benzene or benzoquinone derivatives, including, for example, geldamycin. The maytansinoids isolated from plants, which have cytotoxic effects, are also A. Only the Rifamycins (see) are therapeutically important.

Antabuse®: same as Disulfiram (see).

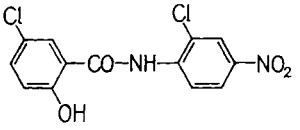
Antacids: compounds or preparations which are used to bind excess hydrochloric acid in the stomach. The pH of gastric juice should be raised to 3.0 to 4.0; in no case should the content of the stomach be neutralized, because in this case more gastric juice will be secreted. This danger is present when carbonates (e.g. magnesium carbonate), hydrogencarbonates (e.g. sodium hydrogencarbonate) or oxides (e.g. magnesium oxide) are used. Colloidal aluminum hydroxide and aluminum magnesium silicates are better for the purpose, because they have a good capacity to bind acid without increasing the pH above 4.0.

Antamanid: cyclo-(Pro-Phe-Phe-Val-Pro-Pro-Ala-Phe-Phe-Pro-), a homodetic, cyclic decapeptide isolated from the death's cap mushroom which can counteract the toxicity of phalloidin (see Phallotoxins) and α-amanitin (see Amatoxins). Reliable protection against the lethal effect of the toxins is only obtained, however, when the protective dose of A. (0.5 mg/kg mouse against 5 mg/kg phalloidin) is ingested before or at the same time as the poison. A. was discovered in 1968 by T. Wieland and coworkers, who also elucidated the structure and synthesized it.

Antarafacial: see Woodward-Hoffmann rules.

Antelepsin®: see Benzodiazepines.

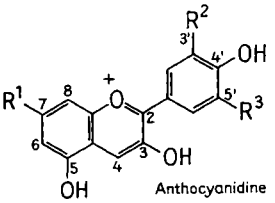
Anthelminthics: compounds used to combat parasitic worms in human beings and animals. They are effective against worms in the gastrointestinal tract, and in some cases, against tissue parasites. Some compounds effective against nematodes (threadworms) and ascarides (eelworms) are piperazine, cyanine dyes (such as pyrvinium embonate), benzimidazol derivatives (e.g. mebendazol) and cyclic amidines (such as pyrantel). At present, the most important medication for cestodes (tapeworms) is the salicylanilide derivative *niclosamide*.



Niclosamide

Anthocyanidins: see Anthocyans.

Anthocyanins: a group of glycosidic plant pigments. The most important of them are cyanin, pelargonin, delphin, idaein, malvin, petunin, keracyanin, micocyanin, fragarin, paeonin, oenin and chrysanthemin. A. are hydrolysed by acids or glycosidases to the corresponding aglycons, the ***anthocyanidins*** (Table), which are flavylium salts. The chlorides are usually dark violet, brown or dark red crystals with m.p. > 300 °C. The natural compounds differ with respect to the number of hydroxyl groups: pelargonidin, cyanidin and delphinidin have one, two and three, respectively. In other anthocyanidins, some of the hydroxyl groups are methylated, as in peonidin, petunidin, malvidin and hirsutidin. In the A., the sugar residues are bound to the 3- or 5-positions of the anthocyanidins: monosaccharides are found at the 3- or, more rarely, the 5-position, or at both positions, or a disaccharide group is present at the 3-position. The most common monosaccharides are glucose and galactose. In addition, the phenolic hydroxyl groups may be acylated with phenol carboxylic acids or other carboxylic acids. For example, the acylated A. of red cabbage contain p-coumaric, ferulaic and sinapic acids.

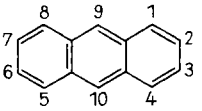


Anthocyanidine

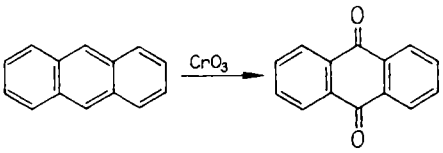
R^1	R^2	R^3	Anthocyanidine
OH	H	H	Pelargonin
OH	OH	H	Cyanidin
OH	OH	OH	Delphinidin
OH	OCH_3	H	Peonidin
OH	OCH_3	OH	Petunidin
OH	OCH_3	OCH_3	Malvidin
OCH_3	OCH_3	OCH_3	Hirsutidin

The A. are common red, violet or blue pigments in blossoms, berries and other parts of the plant. They are responsible for the colors of strawberries, raspberries, blueberries, cherries and plums. The color of the A. depends on pH. Blue A. are present in the plant, e.g. in cornflowers, as Al(III) and Fe(III) complexes which are also bound to polyuronides. A. are used as food colorings.

Anthracene: a condensed aromatic hydrocarbon, one of the acenes. It crystallizes in colorless, blue-fluorescing leaflets which sublime: m.p. 216.3 °C, b.p. 340 °C (subl.). It is insoluble in water, slightly soluble in ethanol and ether, somewhat soluble in boiling benzene. A. is found in coal tar, and is still isolated from it industrially.



It can be synthesized by pyrolysis of 2-methylbenzophenone, by a Friedel-Crafts reaction of 2-bromobenzylbromide, or by reaction of benzene with phthalic anhydride in the presence of aluminum chloride. Only one of the rings in A. has six π-electrons. It is therefore rather reactive, especially at positions 9 and 10. It is easily oxidized here to anthraquinone; addition of nascent hydrogen produces 9,10-dihydroanthracene, and the Diels-Alder reaction with maleic anhydride also occurs readily. The oxidation:

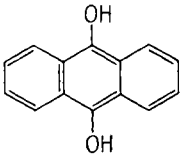


is industrially important.

Electrophilic reagents like sulfuric acid can also attack the 1 or 2 position, so that both anthracene 1-sulfonic acid and anthracene 2-sulfonic acid are formed together. A. is used mainly to produce alizarin and indanthrene dyes; it also serves as starting material for agricultural chemicals and tanning agents.

Anthracene blue: 1,2,4,5,6,8-Hexahydroxyanthraquinone, a pure blue, synthetic pigment; one of the anthraquinone dyes. A. is produced by reaction of mildly fuming sulfuric acid with 1,5-dinitroanthraquinone. It is used to dye wool and cotton.

Anthracene-9,10-diol, ***anthrahydroquinone***: an anthracene diphenol compound. A. forms brown crystals which dissolve in ethanol with a green fluorescence; m.p. 180 °C (dec.).



Anthracene-9,10-diol

A. is synthesized by treating anthraquinone with zinc powder and alkali hydroxide or with sodium dithionite. The alkaline solution of A. is dark red, and the color disappears when the solution is shaken in air, due to oxidation to anthraquinone. The preparation of anthraquinone dyes for use (vatting) depends on the above reduction reactions. The salts of sulfate esters of A. are used for dyeing and printing; they are called anthrasols.

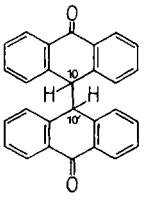
Anthracene oil: see Tar.

Anthracite: a mineral coal at the last stage of carbonization; its vegetable origin can be detected only by polarized-light microscopy. A. is very hard and shiny, and contains only 6 to 10% volatiles. It is difficult to ignite, burns without smoke, and has a low ash content. Its water content is only about 2%. A. is more than 91.5% carbon, less than 3.75% hydrogen and less than 2.5% oxygen. A. has the highest heating value of any coal: up to 35,000 kJ kg^{-1}. When gasified, it yields a powdery residue and an almost tar-free gas. A. is used mainly as a special fuel and reducing agent, and in production of water gas. It is used to produce large electrodes.

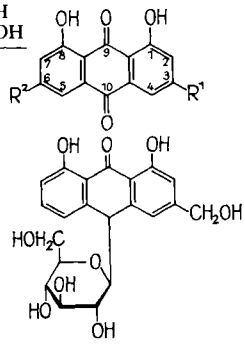
Anthracyclins: a group of antibiotics with anthraquinone derivatives as aglycons. They contain fused linear cyclohexane rings (anthracyclinones). An aminosugar is glycosidically linked to the aglycon. The orange to red A. are formed by various species of *Streptomyces*, e.g. *adriamycin* by *S. peuceticus* and *daunomycin* by *S. coeruleorubidus*. They are used as antineoplastics, for example, in the treatment of acute leukemia. Their activity is due to intercalation of the planar part of the molecule into the DNA of the dividing cell and its fixation in that position by interaction of the amino group with the acidic phosphodiester bonds. Most A. are too toxic for therapeutic applications.

Anthraglycosides: glycosides of hydroxylated derivatives of anthraquinone and its partially reduced relatives, such as anthranols, anthrones and bianthrones. The most important aglycons of the anthraquinone type, which are called *emodins*, are rhein, aloe emodin, chrysophanol and frangula emodin. Similarly substituted aglycons of the anthrone and bianthrone types are also known; in compounds of the dimeric bianthrone type, a single molecule can have two identical or two different substitution patterns on its aglycon rings.

Name	R^1	R^2
Rhein	COOH	H
Aloe emodin	CH_2OH	H
Chrysophanol	CH_3	H
Frangula emodin	CH_3	OH



Bianthrone



Aloin

The most important medicinal plants containing A. are the rhizomes of certain species of rhubarb, senna leaves, buckthorn (black alder, dogwood) bark and various species of aloe. Rhubarb contains anthraquinone, anthrone and bianthrone aglycons, mainly as glucosides. Buckthorn bark contains mainly bianthrone glycosides of the frangula emodin type; these are poorly tolerated, and within a year of storage they are converted by oxidation to anthraquinone compounds. The main active compounds in senna leaves are sennosides A and B. Sennoside A is the (+)-form, and sennoside B, the *meso*-form with a varying configuration at C-9 and C-9'. The most important component of aloe is aloin, the 10-C-glycopyranosyl compound of aloe emodin.

1,8-dihydroxyanthraquinone derivatives are detected by the red color they develop with hydroxide ions (Bornträger's reaction), or sometimes after cleavage of the glycoside bond and oxidation of the corresponding anthrones and bianthrones to anthraquinones.

A. are laxatives which irritate the mucous membrane of the large intestine and increase peristalsis. It is thought that only the anthrone and bianthrone compounds are effective.

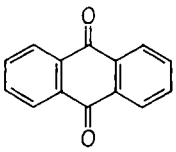
Anthrahydroquinone: same as Anthracene-9,10-diol (see).

Anthralane dyes: a group of acid dyes which are very fast to light and give the fibers (mainly wool) an even color.

Anthranilic acid: see Aminobenzoic acids.

Anthranilic acid methyl ester: $2\text{-}H_2N\text{-}C_6H_4\text{-}CO\text{-}OCH_3$, a colorless, crystalline compound with an odor similar to orange blossoms; m.p. 24-25 °C, b.p. 256 °C. It is slightly soluble in water, and readily soluble in alcohol and ether. A. is found naturally in essential oils, for example jasmine and orange-blossom oil, oil of lemon peel, narcissa oil and bergamotte leaves. It is used in perfumes.

Anthraquinone, ***9,10-dihydroanthracene-9,10-dione***: the quinone derived from anthracene. A. crystallizes in light yellow needles, subl. 286 °C, b.p. 379.8 °C. A. is insoluble in water, and soluble in alcohol, ether and benzene.



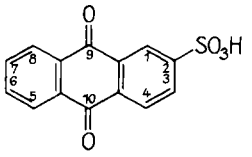
In contrast to most quinones, A. cannot be steam-distilled. It is very stable to oxidation, but is easily reduced to anthrahydroquinone, for example by sodium dithionite. This reaction is the basis of fixing of anthraquinone dyes. Reduction with tin and hydrochloric acid in glacial acetic acid produces anthrone. A. can undergo electrophilic substitution reactions, such as nitration or sulfonation, giving mono- or disubstitution products. For the dye industry, the most important of these are the Anthraquinone sulfonic acids (see). The CO groups of A. react only slightly with the typical ketone reagents. A. is produced by oxidation of anthracene with nitric or chromic acid, or by the Friedel-Crafts reaction of benzene and

phthalic anhydride; the latter method is also suitable for synthesis of substituted A. A. is the key compound for production of Anthraquinone dyes (see); it is also used as a bird repellent.

Anthraquinone dyes: a group of synthetic dyes which are very colorfast, especially with respect to light fading. The ***anthraquinone acid dyes*** have sulfonic acid groups on the anthraquinone nucleus to make them water-soluble; in addition, they contain other ring systems such as acridone and thiazole. The A. are used as vat, mordant and chrome dyes. The anthraquinone vat dyes are a diverse group of compounds, some based on the simple anthraquinone skeleton, but others consisting of several anthraquinone molecules. This group includes some indanthrene dyes.

Anthraquinone acid dyes: see Anthraquinone dyes.

Anthraquinone sulfonic acids: sulfonation products of anthraquinone with one or two sulfonic acid groups in the molecule. Depending on the reaction conditions, sulfonation produces mostly anthraquinone 1-sulfonic acid or 2-sulfonic acid. Further sulfonation produces anthraquinone disulfonic acids, in which the sulfonic acid groups are located at the 1,5- and 1,8- or 2,6- and 2,7- positions. The A. can be converted by melting with alkali to hydroxyanthraquinones; both groups are important intermediates in the dye industry.

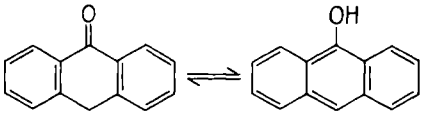


Anthraquinone 2-sulfonic acid

Anthranol: the enol form of Anthrone (see).

Anthra red B: same as thioindigo (see Indigo).

Anthrone: a carbonyl compound derived from anthracene. A. forms pale yellow needles, m.p. 155 °C. It is not soluble in water, but is soluble in alcohol, benzene and acetone. It dissolves in alkali hydroxide solutions when heated, and the tautomeric ***anthranol*** (anthr-9-ol) can be isolated from these solutions after acidification.



Anthrone Anthranol

This type of tautomerism is called *transannular tautomerism*. Anthranol forms orange crystals which fluoresce strongly in solution; m.p. 120 °C. The stable A. is formed by reduction of anthraquinone with tin and hydrochloric acid. It is used in the production of vat dyes and in the determination of carbohydrates.

anti-: see Stereoisomerism 1.2.3.

Antiallergics: see Antihistamines.

Antiandrogens: antagonists of testosterone; the best known is ***cyproterone acetate***. Because of its gestagen effect, this is used as a component of contraceptives. Cyproterone acetate is to treat male hypersexuality and masculinization of women.

Antianginous drugs: see Coronary drugs.

Antiaromatic: see Aromaticity.

Antiarrhythmics: drugs used to relieve cardiac arrhythmia. Quinidine, ajmaline and its derivative detajmium bitartrate, β-receptor blockers, e.g. propanolol and talinolol, and local anesthetics such as lidocain and procainamide, p-H_2N-C_6H_4-CO-NH-CH_2-CH_2-$N(C_2H_5)_2$, are used as A.

Antiauxochromes, ***antiauxochromic groups***: groups such as -NO_2 and >C=O which form resonance structures with Auxochromes (see) in chromogens (see Chromophores) and thus deepen the color of the compound (see Bathochromicity).

Antibase: see Acid-base concepts, Bjerrum definition.

Antibiotics: compounds produced by microorganisms, and their partially or totally synthetic analogs, which at low concentrations can inhibit the growth of other microorganisms. The A. are chemically very heterogeneous. Some of the major classes are: amino acid derivatives (for example, the amino acid antagonists cycloserine and azaserine, the β-lactam and polypeptide A.), aminocyclitols and nucleoside A. Many A. are biosynthesized by the polyketide pathway, such as the macrolide antibiotics, the tetracyclins, griseofulvin and cycloheximide.

Most of the A.-producing organisms are bacteria of the genera *Bacillus* and *Streptomyces* or molds of the genera *Penicillium, Aspergillus* and *Cephalosporium*. Of approximately 5,500 A. which have been isolated from microorganisms, about 4000 are products of actinomycetes. About 300 new A. are reported anually.

For production of A., the microorganisms are grown in suitable nutrient media in surface or submersion culture (fermentation). Production strains with high productivities are used; these are obtained by selection, often after artificially induced mutation of the original strain. Productivity is affected not only by the genetic potential of the cultured organisms, but by the nutrient medium and, for aerobes in submersion culture, by the aeration. After a maximum concentration of A. has been reached, the fermentation is terminated, and the microorganisms are removed by filtration. The culture medium is then processed by methods which depend on the properties of the A. The most common are liquid-liquid multi-step extraction of relatively lipophilic A. with organic solvents (e.g. benzylpenicillin), ion-exchange chromatography of A. with acidic or basic groups (e.g. the aminocyclitols) and perhaps precipitation of insoluble derivatives (e.g. oxytetracycline). In some cases, new A. were obtained by addition of precursors to the nutrient medium (e.g. phenoxyacetic acid for production of phenoxymethylpenicillin). Partial synthesis plays an important role, especially in the production of the penicillins and cephalosporins. Only a few A. are made by total chemical synthesis (e.g. chloramphenicol).

The action spectra of individual A. vary. Most penicillins, erythromycin and the polypeptide antibiotics are only effective against gram-positive bacteria,

while the polymyxins affect only gram-negative bacteria. ***Broad-spectrum A.*** are active against either gram-positive or gram-negative bacteria. This group includes mainly the tetracyclins, chloramphenicol, the cephalosporins and a few partially synthetic penicillins (e.g. ampicillin). Only a few A. affect fungi; griseofulvin and a few polyene A. are used. Some A., including mitomycin, rifamycin and the anthracyclins, inhibit the growth of cancer cells.

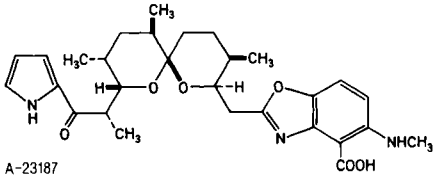
In addition to their use as chemotherapeutics for treatment of human and animal infections, and of malignant tumors, A. are now used in large quantities on plants and in industrial animal production, as additives to feeds. These additives produce higher slaughter weights of the animals.

A problem with the application of A. is that the microbes develop resistance, that is, an inherited insensitivity of certain strains to the A. The resistance can also be transferred from one species to the next on extrachromasomal DNA (plasmids). Biochemically, resistance arises in several ways. The membrane may change so that an otherwise effective A. is no longer absorbed; this type of resistance is observed after tetracyclin treatments. The resistant microbes often form enzymes, usually hydrolases or transferases, which inactivate the A. This is the case in resistance to the β-lactam A. (β-lactamase, penicillinase), chloramphenicol (chloramphenicol acetyltransferase) and aminocyclitol A. (acetyl, phosphate and adenylate transferases). Cross-resistance can develop between A. with related chemical structures.

The mechanisms of action of A. are varied. Some points of attack are DNA (mitomycin, actinomycin, anthracyclins), protein synthesis (chloramphenicol, aminocyclitols, tetracyclins, rifamycin), the membrane (ionophores, polyene A.) and the biosynthesis of the bacterial cell wall (β-lactam A., cycloserine, bacitracin).

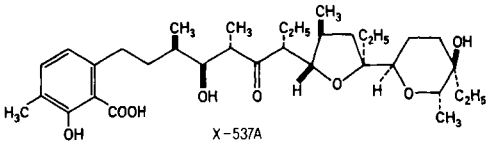
Historical. The first hints of A. were observed in 1877 (Pasteur and Joubert) and 1889 (metabolic product of *Bacillus pyrocyaneus*). In 1929, Fleming discovered penicillin. It was not purified until 1940, however (Florey, Chain). The term A. was introduced by Waksman in 1942. In 1944, streptomycin, the first aminocyclitol A., was obtained (Waksman). The first broad-spectrum A. was chloramphenicol, isolated in 1947, and synthesized shortly thereafter (Rebstock). In 1980, the world production of A. was about 25,000 t, of which about 17,000 t were penicillins, and 5000 t were tetracyclins.

Antibiotic A-23187, ***calcimycin***: a natural ionophore. It is a crystalline powder which is soluble in ethyl acetate, chloroform, methanol and dimethylsulfoxide, but only slightly soluble in water. A. is commercially available as either the free acid or the calcium/magnesium salt. It can transport divalent cations through lipophilic membranes, and binds Mn^{2+} > Ca^{2+} > Mg^{2+} with a relative binding affinity of 210:2.6:1. It is used as a calcium ionophore for studies in cell biology. In vitro, it has a weak effect against gram-positive bacteria.



A-23187

Antibiotic X-537a, ***lasalocide***: an antiobiotic isolated from a streptomycete. It forms colorless crystals; m.p. 100-109 °C, which are soluble in organic solvents but practically insoluble in water. A. is a lipophilic salicylic acid derivative; it acts as a calcium ionophore (see Ionophore).



X-537A

Antibodies: proteins (immunoglobulins) synthesized by vertebrate lymphocytes in response to antigenic stimulation. They bind very specifically to the antigen, often causing it to precipitate (***antigen-antibody reaction***). The A. consist of two light and two heavy peptide chains linked by disulfide bridges. Part of the sequences of these chains are relatively invariant and part of them (the variable regions) are specific for the antigen. There are several different types of heavy chain which account for the different types of A. (Immunoglobulin = Ig): IgA, IgM, IgG, IgE, IgD. IgG is commonly known as γ-globulin because it migrates with the γ-fraction of the blood serum in electrophoretic separations.

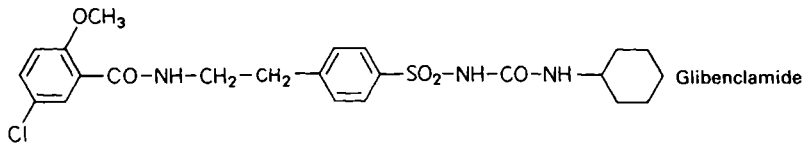
Anti-clinal conformation: see Stereoisomerim, Fig. 14.

Anticoagulants: see Antithrombotics.

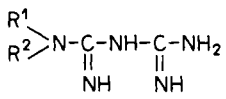
Anticonvulsants, ***antiepileptics***: compounds which prevent the incidence of central nervous system convulsions or reduce their intensities. An epileptic seizure can involve tonic and clonic convulsions (grand mal) or it may not produce generalized convulsions (petit mal). Important A. are found among the barbitals, the hydantions and the succinimides (see Ethosuximide). *Carbamazepin* is another important A. which is also used to treat trigeminus neuralgias.

Antidepressives: Psychopharmaceuticals.

Antidiabetics: drugs used to treat diabetes mellitus. The disease is due to a lack of insulin in the blood, and can be relieved by administration of insulin. Oral A. can be used to treat some forms of diabetes, particularly diabetes of age. This group of compounds includes *N*-arylsulfonylurea and biguanides. The first oral A. was *carbutamide*, 4-NH_2-C_6H_4-SO_2-NH-CO-NH-C_4H_9(n). However, because of its undesirable side effects as a sulfonamide derivative, it is no longer used. Other *N*-arylsulfonylureas with other substituents instead of the aromatic amino group act as A. *Tolbutamide*, 4-CH_3-C_6H_4-SO_2-NH-CO-NH-C_4H_9(n) was the first to become prominent. Replacement of the methyl group on the benzene ring by more hydrophobic groups created much stronger A. such as *glibenclamide*. The compounds listed so far stimulate insulin production in cases where it is inadequate. In rare cases, biguanides such as butylbiguanide (*buformin*) and *metformin* are used; they act by a different mechanism.



Glibenclamide



$R^1 = H$, $R^2 = C_4H_9(n)$: Buformin

$R^1, R^2 = CH_3$: Metformin

Antidiuretic hormone: same as Vasopressin (see).

Antidiuretin: same as Vasopressin (see).

Antidote: a substance which is administered to counteract the effects of a poison. The essential components of treatment for poisoning, in addition to an A., are symptomatic therapy, maintenance of vital life functions, measures to prevent further absorption of the poison and acceleration of its elimination. Occasionally substances which affect absorption or elimination of the poison (emetics, laxatives, adsorptive substances, oxidizing agents) are called unspecific A. However, A. in the narrow sense are specific drugs. Their mechanism of action may be a) chemical: they may convert the poison to an insoluble and therefore non-poisonous compound (e.g. precipitation of soluble barium and lead compounds with sodium sulfate); the soluble poison may be converted to a soluble but non-poisonous compound (e.g. conversion of cyanides into rhodanides by sodium thiosulfate, or binding of cyanide to methemoglobin, which can be formed in the organism by administration of compounds such as nitrites or methylene blue); or acids can be "neutralized" with dilute bases such as sodium hydrogencarbonate, soapy water or magnesium oxide. b) Pharmacological A. counteract the pharmacological effect of the poison, e.g. by competion for cellular receptors as in the case of acetylcholine and atropine. Poisoning by substances which inhibit the degradation of physiologically formed acetylcholine (see Poisons), is actually a form of endogenous acetylcholine poisoning, which can be treated by relatively high doses of atropine. A. can also reactivate enzymes which have been blocked, e.g. cholinesterase inhibited by phosphate esters can be reactivated by pralidoxime (PAM), or enzymes containing thiol groups blocked by metal ions can be rescued by 1,2-dithioglycerol, which binds the metal ions (e.g. mercury, arsenic) more tightly than the endangered enzymes do (Table).

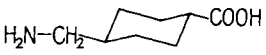
Antidote	Application
Bemegride	Stimulation of the respiratory center after barbiturate poisoning
Biperiden	Neuroleptica poisonings
Atropine sulfate	Cholinesterase inhibitor poisoning
Dexamethasone isonicotinate	Poisoning with phosgene, nitrosulfuric gases and other lung irritants
Calcium thiosulfate	Fluoride, oxalate or citrate poisoning
Methylthionine chloride (methylene blue)	Poisoning by methemoglobin-forming compounds (nitrobenzene, aromatic nitro and amino compounds, nitrites
Deferoxamine mesylate	Iron poisoning
Dimethylaminophenol	Hydrocyanic acid and cyanide poisoning
Clomethiazole	Alcohol delirium
Sodium calcium EDTA	Heavy metal poisoning, esp. by Pb, Ni, Cu, Zn, Cr, Cd, Mn Prophylaxis against heavy metal poisoning
Polystyrolsulfonate resin, Ca form	Potassium poisoning
Dimeticon	Poisonings with tensidine and other foaming agents
Hexamethylenetetraamine	Phosgene poisoning
Isoamylnitrite	Hydrocyanic acid and cyanide poisonings
Pyrostigmine	Anticholinergic (atropine) poisoning
Phytomenadione	Poisoning with indirect coagulants
Nalorphine hydrobromide	Overdoses of morphine or its derivates
Sodium thiosulfate	Hydrocyanic acid or cyanide poisoning
Obidoxime	Alkylphosphate poisonings
Penicillamine	Heavy metal poisoning, esp. by Pb, Hg, Cu, Au, Co, Zn
Protamine sulfate	Heparin poisoning
Dimercaptrol	Heavy metal poisoning, esp. by As, Hg, Au, Ni, Cu, Sn

Antienzymes: polypeptides or proteins which act as enzyme inhibitors. The term includes those antibodies which bind to the enzyme in such a way as to inhibit it, but not those which bind without affecting the activity.

Antiepileptics: same as Anticonvulsants (see).

Antifeedants: see Insect repellents.

Antifibrinolytics: compounds used to treat pathologically activated fibrinolysin and to control therapeutically applied fibrinolysins (streptokinase treatments). They inhibit activation of plasminogen or plasmin, and thus of fibrinolysin, which breaks down polymeric fibrin. ε-Aminocaproic acid, 4-aminomethylbenzoic acid (PAMBA®) and the *trans*-isomer of 4-aminomethylcyclohexane carboxylic acid (tranexamic acid) are used as A.



Tranexamic acid

Antifluorite type: see Fluorite type.

Antifoaming agents, ***foam inhibitors***, ***foam breakers***: substances used to prevent formation of foam. Because they do not mix readily with the foaming liquid, they tend to accumulate on the liquid-gas

interface. Alkylpolysiloxanes are effective for both aqueous solutions and oils in amounts of 0.01 to 0.1%. In lubricating oils, a critical siloxane concentration must be exceeded, because they otherwise act as foam generaters. For aqueous solutions, it is also possible to use higher alcohols, propylene glycol and ethylene oxide-propylene oxide adducts as A.

Antifreeze: materials which are added to water to lower its freezing point, such as methanol, ethanol, ethylene glycol, glycerol, sodium, potassium, calcium or magnesium chloride, or potassium carbonate. They are used in engine coolants, to make cooling brines for refrigeration equipment, in hydraulic systems, to de-ice aircraft and motor vehicles, and in the liquids used to clean streets in winter. A. mixtures often contain corrosion inhibitors (such as borax, phosphates or chromates) and antifoaming agents (e.g. fatty acid esters or silicon oils). A. are used in construction so that concrete can be poured even at low temperatures. Some other special applications are Freezing point lowering (see) of diesel fuels (see Additives) and prevention of icing of carburetors (see Anti-icing agents).

Antigens: substances which induce the formation of Antibodies (see). They are usually foreign to the body; induction of antibodies to the body's own proteins is the cause of autoimmune diseases. A. are most often proteins or polysaccharides with molecular masses greater than 2000. Artificial A. can be synthesized by covalently linking a small molecule, such as a benzene derivative, to a protein.

Antihistamines: compounds which reverse or reduce the physiological effects of histamine. The reduction in blood pressure induced by histamine is mediated by H_1 and H_2 receptors; correspondingly, the A. are classified as H_1 and H_2 antagonists. The classic A., which have long been known, are also called *antiallergics*; these compounds are H_1 antagonists. Examples are *diphenylhydramine* (Diabenyl®), *etholoxamine* (AH 3®), *tripelannamine* (Dehistin®), *talastine* (Ahanon®) and *dioxopromethazine* (Prothanon®). The phenothiazine derivatives promazine and promethazine are used in the same way (see Phenothiazines). The close structural similarities of H_1 antagonists with other types of drugs explains the side effects of these compounds, such as depression of the central nervous system, spasmolysis, sympathicolytic and parasympathicolytic effects and local anesthesia.

The H_2 antagonists were discovered much later than the H_1 antagonists. H_2 antagonists are able to inhibit the histamine-induced secretion of gastric juice. The first compound of this type was *cimetidine*, which is used to treat gastric and duodenal ulcers.

Anti-Hückel system: see Aromaticity.

Antihypertensives: compounds which reduce pathologically high blood pressure. The blood pressure should drop slowly in the course of therapy, and remain within the normal range, without great deviations, during maintenance therapy. In the majority of cases, the cause of the hypertension is unknown (*essential* or *primary hypertension*). *Symptomatic* or *secondary hypertension* is caused by pathological changes in the organs, for example the kidneys (*renal hypertension*) or the endocrine glands. The following A. are used primarily for essential hypertension (see separate entries for each): Clonidine, Methyldopa, Guanethidine, and Dihydralazine. The Rauwolfia alkaloid reserpine is also used, as are β-receptor blockers (see Sympathicolytics), and Diuretics (see) are used for basic therapy.

Anti-icing agents: additives to Fuels (see) to prevent ice formation in the carburetor under conditions of high air humidity and low temperatures. Alcohols, ether, etc. are suitable A.; they are added at a ratio of about 100 ppm fuel.

Antiisotypism: see Isotypism.

Antiknock compounds, ***knock inhibitors***: compounds added to gasoline in small amounts to increase its resistance to Knocking (see). A. must be readily soluble in the fuel and have about the same volatility. They have no effect on the density, boiling, heating value or similar properties of the fuel. The resistance of a gasoline to knocking is expressed by its Octane rating (see). Although normal alkanes tend to cause knocking, iso-alkanes, naphthenes and aromatics are very knock-resistant components of gasoline.

The most effective A. are organometallic compounds, especially tetraethyl and tetramethyl lead, methylcyclopentadienyl tricarbonyl manganese, pentacarbonyl iron and carbonyl nickel. However, N-containing aromatic compounds, such as aniline and xylidine, are also effective. Relative to tetraethyl lead, the amounts of compound required to give the same knock resistance are as follows: Tetraethyl lead, 1; methylcyclopentadienyl tricarbonylmanganese, 1.2; pentacarbonyliron, 3; tetracarbonylnickel, 8; aniline, 90; xylidine, 150. The combustion products of tetraethyllead are poisonous, and in areas with dense traffic, their concentration becomes a health hazard. In addition, these products poison the catalysts used to reduce the other emissions of the engine (unburned hydrocarbons and CO) which are serious environmental contaminants (see Smog). For this reason, unleaded gasolines are required for cars equipped with catalytic converters, which are required by law in many places (see Fuels).

The effect of the metal-containing A. depends on the fact that they decompose thermally in the combustion space before the fuel-air mixture ignites, leading to a finely divided metal or metal compounds, which react with unstable intermediates of "cold combustion" and thus prevent premature ignition of the fuel.

Antimalarial agents: compounds used for therapy and prophylaxis of malaria, a disease which is transmitted by the *Anopheles* mosquito and is very widespread in the tropics. The developmental cycle of the malaria organisms within the human host is very complicated; the asexual schizonts and/or the sexual gametocytes inside and outside the erythrocytes can be the point of attack by A. Some A. can also be used successfully for prophylaxis of malaria. The classical A. is quinine. Some synthetic compounds now used are chloroquine, primaquine, pyrimethamine and proguanil.

Anti-Markovnikov orientation: see Markovnikov rule.

Antimetabolites: chemical compounds which are structurally similar to metabolites, and therefore compete with them for binding sites on enzymes in biochemical reaction chains. They thus block the

metabolic pathways at specific sites. Some examples of A. are the synthetic nucleic acid bases fluorouracil, cytarabin and 6-mercaptopurine; the folic acid A. methotrexate; the *p*-aminobenzoic acid A. *p*-aminosalicylic acid; and the sulfonamides. The nucleic acid A. and methotrexate are used as cytostatics; the sulfonamides are antibiotics, and *p*-aminosalicylic acid is used against the tuberculosis bacillum.

Antimonates: ***Antimonates(III)***, same as Antimonites (see). ***Antimonates(V)***, the salts of antimonic(V) acid, which does not exist in pure, defined form. Antimonic acid and A. differ from phosphoric acid and phosphates in that the antimony is *sixfold* coordinated. Antimonic(V) acid should probably be formulated as $H[Sb(OH)_6]$, so that the A. are more correctly called ***hexahydroxoantimonates(V)***, $M^I[Sb(OH)_6]$. Most of these salts are relatively insoluble in water; they are obtained by melting the metal hydroxides with antimony(V) oxide. Potassium hexahydroxoantimonate, $K[Sb(OH)_6]$, is used as a precipitating reagent for sodium ions.

Antimonic acid: see Antimony oxides; Antimonates.

Antimonites, ***antimonates(III)***: the salts of antimonous acid, $HSbO_2$, which does not exist in the free state. The A. are made by dissolving antimony(III) oxide in alkali hydroxide solutions, e.g. $Sb_2O_3 + 2\,KOH \rightarrow 2\,KSbO_2 + H_2O$. They are strong reducing agents.

Antimonous acid: see Antimonites.

Antimony, ***stibium***, abb. ***Sb***: an element of the 5th main group of the periodic system, the Nitrogen-phosphorus group (see). Sb is a semimetal, *Z* 51. The natural isotopes have mass numbers 121 (57.25%) and 123 (42.75%); the atomic mass is 121.75. Sb has valences III and V; its Mohs hardness is 3, density 6.684, m.p. 630.5 °C, b.p. 1750 °C, electrical conductivity 2.56 Sm/mm^2 at 0 °C, standard electrode potential 0.1445 V ($2\,Sb + 3\,H_2O \rightleftharpoons Sb_2O_3 + 6\,H^+ + 6\,e$).

Properties. Gray A. is a silvery white, shiny, very brittle and readily pulverized metal. Its lattice corresponds to that of gray metallic arsenic. Other modifications described in the older literature, such as yellow A., black A. or the glassy-amorphous explosive A. are now considered uncertain or have been shown to be multi-component systems. A. vapor consists of Sb_4 molecules, which dissociate into Sb_2 units at higher temperatures. Above its melting point, A. burns in air to form antimony(III) oxide, Sb_2O_3. In finely divided form, it burns in chlorine to antimony(V) chloride, $SbCl_5$. Its position in the electrochemical potential series is such that it is not attacked by non-oxidizing acids; nitric acid oxidizes A. to Sb_2O_3 or Sb_2O_5, depending on its concentration. In melts with sulfur, A. forms the antimony sulfides Sb_2S_3 and Sb_2S_5.

The increasing stability of the +3 oxidation state observed in the progression from phosphorus to arsenic is continued to A., and antimonates(V) are strong oxidizing agents, especially in acid solution. In aqueous solution, antimony(III) salts typically form SbO^+ cations.

Analysis. In systematic qualitative analysis, A. is precipitated with the H_2S group in the form of a sulfide which is soluble in ammonium sulfide. After removal of other elements, it is identified as the red-orange Sb_2S_3. The Marsh test produces a metal mirror which is insoluble in hypochlorite solution. Iodometric or bromatometric methods can be used for quantitative analysis, or, for low concentrations, atomic absorption spectroscopy.

Occurrence. The fraction of A. in the earth's crust is 10^{-4}%. It is occasionally found in the elemental state in nature, but antimony sulfides and oxides and metal antimonides are much more common. The important minerals are antimonite (antimony glance, stibnite), Sb_2S_3 and its weathering product, valentinite (antimony bloom), Sb_2O_3, antimony blende, $2\,Sb_2S_3 \cdot Sb_2O_3$, and the antimonides breithauptite, NiSb, and discrasite, Ag_2Sb.

Production. The metal is usually produced from the sulfide, Sb_2S_3. This is either roasted to the oxides Sb_2O_3 or Sb_2O_4 and then reduced to A. with carbon, or it is only partially roasted and the oxide reacts directly with the remaining sulfide, corresponding to the equation $3\,Sb_2O_4 + 2\,Sb_2S_3 \rightarrow 10\,Sb + 6\,SO_2$.

Applications. Pure A. is of little commercial significance. It is used mainly as a component of alloys of tin and lead, which it makes harder (see Tin alloys, Lead alloys). A few organic A. compounds are used in medicine, in particular in the treatment of tropical diseases.

Historical. A. was known 3000 years ago in China, and later in Babylon. The Greeks and Romans used stibnite for makeup to darken their eyelids and lashes. Around 1600, the Frankenhäuser salt dealer Thölde wrote a book, *Triumphwagen des Antimonii*, in which the production of the metal, its uses in alloys and the synthesis of a few derivatives were described.

Antimony butter: see Antimony chlorides.

Antimony chlorides: ***Antimony(III) chloride, antimony trichloride, antimony butter***, $SbCl_3$, colorless, soft rhombic crystals which fume in moist air, M_r 228.11, density 3.140, m.p. 73.4 °C, b.p. 283 °C. $SbCl_3$ is soluble in ether. With a small amount of water, it forms a clear solution, but at higher dilutions, insoluble oxygen chlorides, SbOCl and $Sb_4O_5Cl_2$, precipitate. The salt is obtained by dissolving antimonite in concentrated hydrochloric acid, or by chlorination of antimony. It is used as a caustic in medicine and as a catalyst in organic synthesis.

Antimony(V) chloride, antimony pentachloride, $SbCl_5$, is a colorless liquid when pure; usually, however, it is pale yellow. M_r 299.02, density 2.336, m.p. 2.8 °C, b.p. 79 °C at about 3 kPa. In the gas and solid states, it consists of trigonal bipyramidal $SbCl_5$ molecules. When heated, $SbCl_5$ decomposes to $SbCl_3$ and chlorine. It is hydrolysed in water to antimony(V) oxide hydrates. $SbCl_5$ reacts with many metal chlorides to form hexachloroantimonates, $M^I[SbCl_6]$. It is a strong Lewis acid and forms addition compounds with many donor molecules (e.g. $SbCl_5 \cdot OPCl_3$). It is made by chlorination of $SbCl_3$. $SbCl_5$ is used as a strong chlorinating reagent and as a catalyst in organic syntheses.

Antimony electrode: an oxide electrode used as an indicator electrode in the measurement of pH. The electrode consists of metallic antimony, the surface of which is coated with a thin layer of antimony(III) oxide, Sb_2O_3. The potentiometric reaction is: $Sb + 3\,H_2O \rightarrow Sb(OH)_3 + 3\,H^+ + 3e$. The reversible electrode voltage is thus $E = E^o + (RT/3F)\ln a_{H^+}{}^3$,

that is, $E = -0.059 \cdot pH$. Here E° is the standard electrode potential, R, the gas constant, T, the temperature in kelvin, F, Faraday's constant and a_{H+}, the activity of the hydrogen ions. A. can be used to measure pH from 3 to 11. Its advantage is its excellent mechanical stability (especially compared to gas electrodes), and its disadvantage is its slow response time and its sensitivity to redox systems present in the solution.

Antimony fluorides: ***Antimony(III) fluoride, antimony trifluoride***, SbF_3, colorless, rhombic crystals, M_r 178.75, density 4.379, m.p. 292 °C, sbl.p. 319 °C. SbF_3 is slowly hydrolysed in water. It is made by dissolving antimony(III) oxide in concentrated aqueous hydrofluoric acid.

Antimony(V) fluoride, antimony pentafluoride, SbF_5, is a colorless, oily compound with trigonal bipyramidal molecules; M_r 216.74, density 2.99, m.p. 7 °C, b.p. 149.5 °C. As a strong Lewis acid, SbF_5 forms stable complexes with many organic and inorganic donor compounds. It reacts with metal fluorides to form hexafluoroantimonates, $M^I[SbF_6]$. SbF_5 is most conveniently synthesized by the reaction of anhydrous hydrofluoric acid with antimony pentachloride. Both A. are used as fluorinating reagents in organic synthesis.

Antimony hydride: see Stibane.

Antimony oxides: ***Antimony(III) oxide, antimony trioxide***, Sb_2O_3, M_r 291.50, exists in two modifications which occur naturally as well. In the form which is stable at room temperature, the $[SbO_3]$ pyramids are linked in infinite double chains. This form is converted at 606 °C to a cubic form, which is built up of tetrahedral Sb_4O_6 units; these are also present in the vapor. The molecular structure is like that of P_4O_6; see Phosphorus oxides. The high-temperature modification melts at 656 °C, and sublimes 1550 °C. Sb_2O_3 is amphoteric, dissolving in alkali hydroxides with formation of antimonites: $Sb_2O_3 + 2\,M^IOH \rightarrow 2\,M^ISbO_2 + H_2O$. It dissolves in sulfuric or hydrochloric acid to form antimony(III) sulfate, $Sb_2(SO_4)_3$ or antimony(III) chloride, respectively. Sb_2O_3 is obtained by roasting antimonite, Sb_2S_3, or by burning antimony. It is used as an opacifier in the production of enamel.

Antimony(V) oxide, antimony pentoxide, Sb_2O_5, is a yellow, cubic, crystalline powder; M_r 323.50, density 3.80, Above 330 °C, it loses oxygen and is converted to Sb_2O_4. Aqueous suspensions of the rather insoluble Sb_2O_5 are acidic, but a defined antimony(V) acid is not known. The products which were formerly called antimonic acids, obtained, for example, by hydrolysis of antimony(V) chloride, are not exactly defined, especially with respect to their water contents, and are more correctly termed ***antimony(V) oxygen hydrates***. Sb_2O_5 reacts as the anhydride of this hypothetical acid, for example, by forming potassium hexahydroxoantimonate, $K[Sb(OH)_6]$ with potassium hydroxide (see Antimonates). Sb_2O_5 is made by dehydration of the oxide hydrate, which is formed by oxidation of antimony with concentrated nitric acid.

Antimony(III,V) oxide, Sb_2O_4, is a colorless rhombic or monoclinic crystal powder which is only slightly soluble in water; M_r 307.50. It is made by heating Sb_2O_5 or Sb_2O_3 in the air. Above 930 °C, it releases oxygen and is converted to Sb_2O_3.

Antimony sulfides: ***Antimony(III) sulfide, antimony trisulfide***, Sb_2S_3, red-orange, amorphous powder; M_r 339.69, density 4.12, m.p. 550 °C, b.p. about 1150 °C. When heated in the absence of air, Sb_2S_3 is converted to a rhombic, gray-black modification. It is only slightly soluble in water and dilute acids, but dissolves in ammonium sulfide, forming thioantimonites: $Sb_2S_3 + 3\,S^{2-} \rightarrow 2\,SbS_3^{3-}$; in ammonium polysulfide solution, it is oxidized to thioantimonates; $Sb_2S_3 + 2S + 3\,S^{2-} \rightarrow 2\,SbS_4^{3-}$. It is obtained by passing hydrogen sulfide through an acidified solution of Sb(III) or also by fusing the elements . SbS_3 is found in nature as antimonite (antimony glance, stibnite).

Antimony(V) sulfide, antimony pentasulfide, gold sulfide, Sb_2S_5, a yellow-orange powder; M_r 403.82, density 4.12, dec. 75 °C. Sb_2S_5 is only slightly soluble in water and dilute acids, and reacts with ammonium sulfide solution to give thioantimonates. It is made by fusing the elements .

The A. are used as pigments, in the vulcanization of rubber, in fireworks and in matches.

Antimycotics: compounds with more or less specific effects on fungal infections. Certain disinfectants, such as halogenated phenols, 8-hydroxyquinoline derivatives, invert soaps and triphenylmethane dyes are used as A. Thiocarbamide esters such as tolnaftate (Bocima®), dibenzthione [tetrahydro-3,5-bis(phenylmethyl)-2*H*-1,3,5-thiadiazine-2-thione], imidazole derivatives, such as clotrimazol, and compounds such as miconazol are also used. Certain antibiotics, such as the polyenes amphotericin B and nystatin, and griseofulvin, also have antimycotic effects. Most A. are suitable only for local application. There are no generally reliable systemic A. available at present. Under certain conditions, amphotericin B and miconazol can be used for generalized mycoses. Applied orally, griseofulvin is effective against some fungal diseases of the toes and fingernails. A. are called ***fungistatics*** when they only inhibit growth of the fungus; and ***fungicides*** if they kill the fungi.

Antineoplastics: same as Cytostatics (see).

Antineuritic vitamin: same as Vitamin B_1 (see).

Antioxidants: substances which inhibit oxidation of readily oxidized materials such as mineral, transformer and turbine oils, jet fuels, plastics, rubber, edible fats and soaps.

In food chemistry, A. are substances which improve the shelf life of certain foods, especially fats and fat-containing foods, by preventing their oxidation (which leads to rancidity). A. can be natural components of the foods (tocopherols) or synthetic additives (e.g. gallates, nordihydroguajaretic acid, butylhydroxyanisole).

See also Additive, 1 (petroleum chemistry).

Antiparkinson's agents: compounds which at least partially and temporarily relieve the symptoms of Parkinson's disease, such as the trembling of the limbs, slowing of the gait and stiffness. In some forms of Parkinson's disease, the amount of the inhibitory transmitter Dopamine (see) in the brain stem is reduced. To increase the dopamine content, its biosynthetic precursor, *levodopa (L-dopa, L-3,4-dihydroxyphenylalanine)* is administered; in contrast to dopamine, L-dopa is able to cross the blood-brain barrier. In the brain, it is decarboxylated to

dopamine. L-Dopa is often administered together with a decarboxylase inhibitor, which inhibits its conversion to dopamine outside the brain. Amantadine (see), which was introduced as a virostatic, acts as an indirect dopamine agonist and increases its availablity.

Parasympathicolytics (anticholinergics) are used to suppress the excitatory transmitter acetylcholine. The tropa alkaloids, such as atropine and scopolamine and plant extracts containing them were formerly used. Today the drugs of choice are basic ethers of benzhydrol, such as *ethylbenzhydramine* (Antiparkin®), aminopropanol derivatives such as *trihexyphenidyl* (Parkopan®) and triperidene (Norakin®), and the thioxanthene derivative metixene.

Antiparticles: see Elementary particles.

Anti-periplanar conformation: see Stereoisomerism, Fig. 14.

Antipermeability factor: same as Rutin (see).

Antiphlogistics: compounds which reduce inflammation. They are used in rheumatic diseases, sometimes over long periods of time. Many weak Analgesics (see) are also used for their antiphlogistic activity, for example, derivatives of salicylic acid. More recently, pyrazolidindione derivatives, such as phenylbutazone and kebuzone, the indole derivative indometacin and aralkylcarboxylic acids, such as ibuprofen have been introduced as A. Glucocorticoids are also major A. Gold compounds and chloroquine (which was introduced as an antimalarial) are also used for long-term therapy.

Antiprotozoics: compounds used in the treatment and prophylaxis of protozoan infections. Protozoa which are pathogenic in human beings include, for example, the malaria plasmodia, the sleeping-sickness trypanosomes, the enteroamebas which cause diarrhea, and the trichomonads, which cause trichomoniasis and leishmanias such as kala azar. Quinine and various synthetic drugs are used as Antimalarial agents (see). Suramin was developed for use against sleeping sickness, but has now been replaced by other drugs, such as the bisamidines (pentamidine). The ipecuacuanha alkaloid (-)-emetin is effective against amebic infections. Trichomoniasis is treated with nitroimidazol derivatives, such as metronidazol. Leishmanias are treated chiefly with organic compounds of pentavalent antimony.

Antipsychotics: see Psychopharmaceuticals.

Antipyretics: compounds which reduce fever by their action on the heat center of the central nervous system. Many weak analgesics, such as derivatives of salicylic acid, pyrazolone and aniline analgesics act as A.

Antipyrin®: see Pyrazolone.

Antiseptics: see Disinfectants.

Antistatics: preparations which reduce the static charge on synthetic textile fibers. Most A. are surface active substances, which are applied to the fibers in aqueous solution and form a film on their surface with the hydrophobic groups adjacent to the surface of the fiber and the hydrophilic groups pointing toward the air. These hydrophilic groups are able to take up moisture from the air, so that as a result of ionic mobility, electric charges can be quickly discharged. Furthermore, the A. act as lubricants and reduce the formation of triboelectricity.

Anti-Stokes lines: see Raman spectroscopy.

Antique purple: an animal dye from the juice of the purple snail *Murex brandaris* which was highly prized in antiquity (it was the imperial color in Rome). Structurally, P. is 6,6'-dibromoindigo (see Indigo dyes).

Antisymmetry: A property of the wavefunction Ψ of a multi-electron system with respect to exchange of electron coordinates. The wavefunction must be antisymmetric, that is, its sign must change if the numbering of the coordinates of two electrons is reversed: $\Psi(1,2) = -\Psi(2,1)$. For a system containing two electrons, this is achieved by writing the wavefunction in terms of the orbital spin functions φ_1 and φ_2: $\Psi(1,2) = \varphi_1(1)\varphi_2(2) - \varphi_1(2)\varphi_2(1)$. In the general case, this requirement is fulfilled by writing the wavefunction as a matrix in which every row contains all the orbital spin functions of electron coordinates with the same number *i*:

$$\Psi(1,2,3) = N \begin{vmatrix} \varphi_1(1)\varphi_2(1)\varphi_3(1) \\ \varphi_1(2)\varphi_2(2)\varphi_3(2) \\ \varphi_1(3)\varphi_2(3)\varphi_3(3) \end{vmatrix}$$

N is the normalization factor (see Normalization conditions). Exchanging electron coordinates means exchanging two rows of the matrix, which changes its sign. The antisymmetry requirement is the basis of the Pauli principle.

Antithrombotics: compounds which prevent formation of fibrin, and thus of blood clots (***anticoagulants***), or are able to dissolve clots which have already formed (***fibrinolytics***). 4-Hydroxycoumarin derivatives, such as dicoumarol, ethyl biscoumacetate, phenprocoumon and warfarin; alkylindanediones, such as chlorindione; and heparin and heparinoids are used as anticoagulants. Hydroxycoumarins and arylindanediones inhibit the synthesis of coagulation factors, and are therefore called *indirect anticoagulants*. Heparin activates coagulation factors which inhibit thrombin, and is thus a *direct anticoagulant*. Streptokinase and urokinase are used as fibrinolytics.

Anticoagulants are used as Rodenticides (see).

Antonov's rule: the surface tension between nonmiscible liquids (σ_{12}) is equal to the difference between the surface tensions of the two with respect to air: $\sigma_{12} = \sigma_1 - \sigma_2$. This empirical rule applies only when the mutual interaction is due only to London forces (see Van der Waals bonding forces) and the contributions of the London forces to the surface tensions of the two liquids are equal. Complete spreading of the liquids is also a requirement.

Ant toxins: poisons produced by ants which have a special poison gland; they are used for attack or defense. Most A. are not dangerous to human beings. The longest known is highly concentrated formic acid, which is used by some Formicidae; in the red forest ant *Formica rufa*, for example, the formic acid concentration is 70%. It acts as a respiratory poison in lower animals. Some ants have a poisonous sting. An example is the use of a mixture of various piperidine derivatives which are highly insecticidal by the fire ant (*Solenopsis saevissima richteri*). Others (*Dolichoderiae*) produce poisons in separate anal glands; these have both antibiotic and insecticidal effects. Examples are iridomyrmecin or ketene-dialdehyde mixtures. The Poneridae have a highly devel-

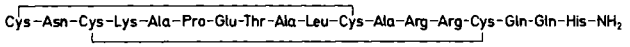
oped poison apparatus with a sting for hunting prey. Little is known about the poisons used by the migratory and driver ants; they contain little or no formic acid and are similar in effect to bee and wasp toxins.

ANTU: a Rodenticide (see).

Antu: see α-Naphthylthiourea.

AO: abb. for atomic orbital.

Apamine: a heterodetic cyclic branched 18-peptide amide with two intrachain disulfide bonds. A. is the neurotoxic component of bee venom. It was isolated in 1965 and its structure was elucidated two years later by Habermann and coworkers.



Apholates: see Chemical sterilizers.

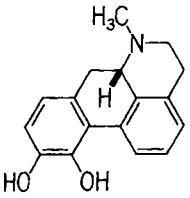
Aphrodisiacs: substances which are supposed to increase the sex drive. Formerly various plant parts were recommended, and also yohimbine.

Apigenin: see Flavones.

Apoatropine: see Atropine.

Apoenzyme: the protein part of an enzyme which requires a covalently bound coenzyme (a low-molecular-weight organic compound) or cofactor (such as a metal ion) for activity. The A. and coenzyme or cofactor together form the holoenzyme.

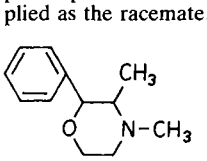
Apomorphine: a product of the reaction of morphine with concentrated sulfuric acid at 150 °C; m.p. 195 °C. The compound is a pyrocatechol derivative which is oxidized in the air and becomes discolored. A. is administered parenterally as a rapidly acting emetic.



Aposafranines: see Azine pigments.

Appearance voltage: the minimum voltage required for formation of fragment ions in Mass spectroscopy (see). It exceeds the ionization potential by an amount equivalent to the dissociation energy of the broken bond(s).

Appetite suppressants, ***anorexics***: compounds which reduce appetite and thus reduce food intake. Under medical supervision, they can therefore be used to reduce body weight. As a rule, A. also excite the central nervous system. Many are derivatives of β-phenylethylamine, and are related to the Sympathicomimetics (see). *Norpseudoephedrin (Exponcit®)*, C_6H_5-CH(OH)-CH(CH_3)-NH_2 and *phendimetrazine (Sedafamem®)* are examples of A. Norpseudophedrin has a *threo*-configuration and is applied as the racemate.



Phendimetrazine

Aprobarbital: see Barbitals, table.

Aqua complexes (also commonly called ***aquo complexes***): metal complexes which contain water, H_2O, as a ligand. Di- and trivalent ions of the metals in the 3d series form A. with coordination numbers of six, $[M(H_2O)_6]^{n+}$ (n = 2 or 3). A. with higher coordination numbers are formed by heavier transition metals, for example the lanthanides. Due to hydrolysis, A. are acidic in aqueous solution: $[M(H_2O)_6]^{n+} + H_2O \rightleftarrows [M(H_2O)_5OH]^{(n-1)} + [H_3O]^+$.

Aquametry: general term for methods of quantitative determination of water in solid and liquid, inorganic and organic substances. These determinations are now made almost exclusively with Karl-Fischer solution (see) as titrant.

Aqua regia: "water of kings", so called because it can dissolve gold, the royal metal. A mixture of 3 parts concentrated hydrochloric acid and 1 part concentrated nitric acid. The two acids react with each other to form chlorine, nitrosyl chloride and water: $3\,HCl + HNO_3 \rightarrow 2\,Cl + NOCl + 2\,H_2O$. Most metals, including gold, are dissolved by the nascent chlorine and the nitrosyl chloride: $Au + 2\,Cl + NOCl \rightarrow AuCl_3 + NO$.

Aquo complexes: see Aqua complexes.

Aqua oxides: same as Oxide hydrates (see).

Ar: 1) symbol for argon. 2) abb. for aryl-.

Ara: abb. for arabinose.

Arabans, ***arabinans***: polysaccharides made up of L-arabinose. A. are found, for example, in Pectin substances (see) and various plant Gums (see).

arabino: prefix indicating a certain configuration, especially in Monosaccharides (see).

Arabinose abb. ***Ara***: a pentose (monosaccharide with five carbon atoms). A. is a colorless powder with a slightly sweet taste which dissolves readily in water and is practically insoluble in organic solvents. ***L-A.***: m.p. 158-160 °C, $[\alpha]_D$ after mutarotation, +104.6°. A. is found naturally as the L- form and more rarely as the D-form. It is a component of plant heteropolysaccharides (arabans, arabinogalactans, arabinoxylans, etc.).

Arachidonic acid: all-*cis*-5,8,11,14-eicosatetraenoic acid, abb. Δ_4Ach or 20:4(5,8,11,14). $H_3C(CH_2)_3(CH_2CH{=}CH)_4(CH_2)_3COOH$ is a polyunsaturated, essential fatty acid. It is a pale yellow liquid, m.p. - 49.5 °C, which is very easily oxidized. Human fat tissue contains 0.3 to 0.9% A. It is enriched in the phospholipids of the brain and liver, where it is bound preferentially to phosphatidylethanolamine. It is the most effective fatty acid in correcting the symptoms of essential fatty acid deficiency. A. is released from glycerophospholipids in cell membranes by the enzyme phospholipase A_2. It is the starting material for biosynthesis of the eicosanoid hormones (thromboxanes), as it is a substrate for the cyclooxygengenases and lipoxygenases. A. is used to treat skin diseases.

Arachinic acid: same as Eicosanoic acid (see).

Arboricide: see Herbicides.

Arbutin, ***hydroquinone β-D-glucopyranoside***: a hydroquinone glucoside which occurs widely in plants,

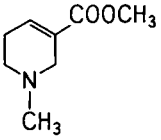
especially the Ericaceae. A. forms colorless, bitter-tasting crystals, m.p. 200 °C, $[\alpha]_D^{20}$ - 64.3°. A. and methylarbutin are the major active components of bearberry leaves, which as a dried medicinal herb should contain at least 6% A. The herb is used to treat infections of the urinary tract; after oral intake, the hydroquinone is present in the alkaline urine and kills the bacteria.

Arc spectra: see Atomic spectroscopy.

Ardein fibers: a Protein fiber (see).

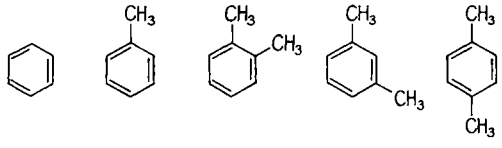
Areca alkaloids: basic substances present at 0.2 to 0.5% in the seeds of *Areca catechu* (betel nut), a tropical palm. The main alkaloid is Arecolin (see). The betel nut is used in Southeast Asia and East Africa and a mild intoxicant.

Arecolin: an areca alkaloid; a very basic oil; b.p. 209 °C. A. is very toxic. It reacts with the acetylcholine receptors and acts as a parasympathicomimetic. A. is used in veterinary medicine as a wormer.



Arene, ***aromatic hydrocarbon***: a cyclic, conjugated compound based on the benzene ring, generally with a relatively low energy content and high stability. The A. are classified on the basis of their structures into monocyclic and polycyclic A. The ***monocyclic A.*** include benzene and its homologs (alkyl benzenes, e.g. toluene); the ***polycyclic A.*** are further subdivided into hydrocarbons in which two or more rings are directly linked (e.g. biphenyl), di- and polyarylalkanes (e.g. diphenylmethane or triphenylmethane) and hydrocarbons with fused rings, one or more of them benzoid in nature (e.g. naphthalene or anthracene).

Fig. 1. Monocyclic arenes



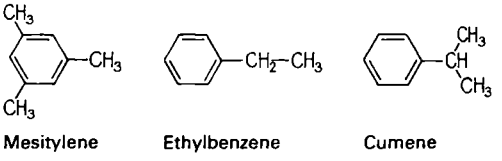
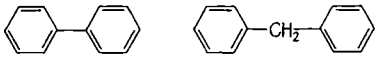
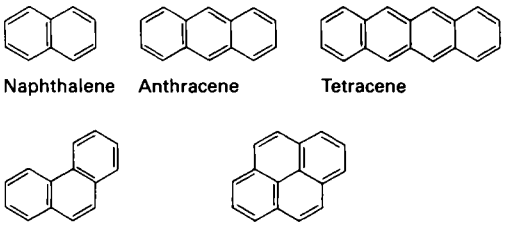
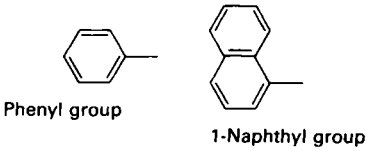


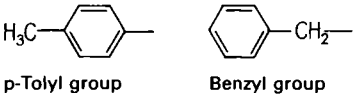
Fig. 2. Polycyclic arenes





Most A. are designated by allowed trivial names. This applies in some cases even to homologs of benzene which might rationally be named as alkyl-, dialkyl-, trialkylbenzene, etc. If a ring system has more than one substituent, these are assigned the lowest possible numbers, as with 1,2-dimethylbenzene (*o*-xylene). For isomeric disubstituted molecules, the prefixes *ortho-* (*o-*) indicates 1,2-; *meta-* (*m-*) indicates 1,3-; and *para-* (*p-*) indicates 1,4-. Formal removal of an H atom from the arene ring produces an ***aryl*** group, such as phenyl-, *p*-tolyl-, 1-naphthyl-, etc.; these should not be confused with the benzyl group which is derived from toluene by removal of an H atom from the methyl group (Fig. 1). The phenyl group is important in nomenclature of polycyclic A.; the benzyl group is used in the names of many compounds which are formally derived from toluene, such as benzyl alcohol, benzyl cyanide, etc. The names of complicated fused rings are constructed in the same manner as those of comparable heterocycles (see Nomenclature).



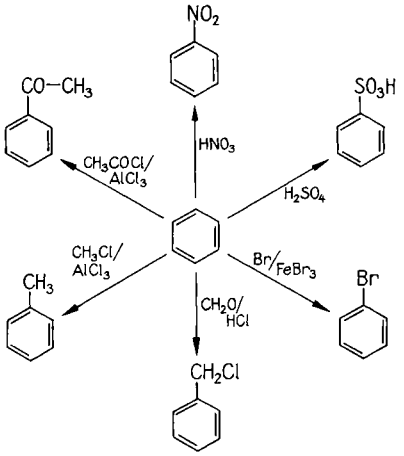


Properties. Monocyclic A. are colorless, flammable liquids which produce large amounts of soot when they burn. They are essentially insoluble in water, but are miscible with various organic solvents, and are themselves very good solvents for fats and oils. Polycyclic A. are generally colorless, crystalline solids, some of which have characteristic odors (naphthalene, for example). They are much less flammable than monocyclic A. Many have a characteristic UV fluorescence, while others absorb visible light and are therefore colored (for example, tetracene, pentacene, coronene). They are insoluble in water. Because of their special bonding and electronic structures (see Aromaticity), the monocyclic A. have considerable delocalization energies, which makes the aromatic ring system very resistant to attack, even by aggresive reagents. For example, these compounds are not destroyed by concentrated sulfuric or nitric acid, unlike the alkanes. Instead, they undergo typi-

cal electrophilic substitution reactions which may be used for their analysis, or are of general importance for syntheses. In fused ring systems, similar substitution reactions are possible, with certain ring positions being favored. Only benzoid rings are inert to hydrogenation, that is, in naphthalene, for example, one of the two rings can be relatively easily hydrogenated (see Tetralene). In anthracene and phenanthrene, the middle rings are relatively easily hydrogenated or oxidized (see Anthraquinone and Phenanthroquinone).

Electrophilic substitutions are the typical reactions of the A.; they conserve the benzoid ring system (Fig. 3).

Fig. 3. Reactions of arenes



Halogenation occurs in the presence of iron(III) halide as catalyst on mild heating; substitution of a halogen atom for an H in the arene ring produces an ***aryl halide (haloarene)***. In the presence of excess halogen, and with strong heating, two or three halogen atoms can be introduced; these are always ortho or para to each other. The formation of structural isomers is governed by substitution rules which are based on the S_E mechanism. Only Cl or Br atoms can be introduced in this way; F and I atoms must be introduced in a series of steps, because their activities are too high and too low, respectively (see Sandmeyer reaction). The reaction conditions required for chlorination or bromination depend on the structure and reactivity of the A.

2) *Nitration*, a reaction with concentrated nitric acid or a mixture of nitric with concentrated sulfuric acid (nitrating acid) occurs at room temperature, or slightly above or below it, depending on the reactivity of the A. *Nitroarenes* are made by substitution of nitro groups for one or more H atoms in the ring system.

Toluene reacts much more readily than benzene, which can be seen from the fact that it can easily be converted to 2,4,6-trinitrotoluene. In contrast, only two nitro groups can easily be introduced into the benzene molecule (1,3-dinitrobenzene).

3) *Sulfonation* can be carried out with concentrated sulfuric acid at room temperature or a little above it. Substitution of an H atom produces the strongly acidic sulfonic acids, most of which are soluble in water. In general, sulfonic acid groups can be introduced to increase the water solubility of many derivatives of the A., such as dyes. In addition, the sulfonic acid group may later be changed to a derivative (see Sulfonamides).

4) In *hydroxymethylation*, the A. reacts with formaldehyde to form a hydroxymethylarene, C_6H_5-CH_2OH. With relatively inert A., such as benzene, the reaction requires an acidic catalyst, such as hydrogen chloride. However, the reaction then often produces a chloromethylarene, polysubstituted products or even condensation products. These reactions are industrially important for the production of plastics from phenols and formaldehyde. Homologous aliphatic or aromatic aldehydes can also be used: C_6H_6 + R-CHO → C_6H_5-CHOH-R.

5) *Formylation reactions* produce aromatic aldehydes in which an H atom of the arene ring is replaced by the aldehyde group (see Gattermann synthesis, Gattermann-Koch synthesis and Vilsmeier-Haack reaction). These reactions, however, are limited to especially reactive A. ("activated A."), and cannot be carried out with benzene, for example.

6) *Nitrosylation*, a reaction with nitrous acid, is also possible only with activated A. such as phenols or tertiary aromatic amines; it introduces a nitroso group para to the activating substituent:

$$R\text{–}C_6H_5 + HNO_2 \xrightarrow{-H_2O} R\text{–}C_6H_5\text{–}NO.$$

Similarly, azo coupling with diazonium salts, which gives azo dyes, and carboxylation with carbon dioxide (see Kolbe-Schmitt synthesis), which gives carboxylic acids, give practical yields only with activated A.

7) *Reactions with alkyl halides* (see Friedel-Crafts reactions).

8) *Chloromethylation* (see Blanc reaction). Substitution of a nucleophile for an H atom in the arene ring is extremely difficult, and is practically never done. However, SN reactions are possible with various substituted A., if suitable leaving groups are present. These include halogen atoms, sulfonic acid groups and the diazonium group, which readily cleaves off nitrogen (see Sandmeyer reaction).

Oxidation reactions are possible with many alkyl arenes and fused ring systems, for example the oxidation of toluene to benzoic acid or *p*-xylene to terephthalic acid.

The classic oxidizing agents, chromium(VI) compounds in glacial acetic acid or sulfuric acid, or potassium permanganate in alkaline solution, are used. Industrially, aromatic carboxylic acids are produced in large amounts by air oxidation in the presence of vanadium(V) oxide or cobalt salts of methylbenzenes. A. can be reduced, with catalytically activated hydrogen under pressure and at high temperatures, to saturated cyclic ring systems; for example, benzene to cyclohexane or naphthalene to decahydronaphthalene. This property is utilized in industry and in the laboratory to synthesize compounds which are otherwise difficult to produce. Usually such reactions require a pressure vessel (autoclave).

Analytical. A. are detected by nitration and reac-

tion with aluminum chloride and chloroform (Friedel-Crafts reactions). They are identified either by sulfochlorination (reaction with chlorosulfonic acid) followed by aminolysis, or by formation of adducts with picric acid. A. with alkyl side chains can be oxidized with potassium permanganate in alkaline solution to carboxylic acids; a few A., such as anthracene or phenanthrene, are oxidized by chromium(VI) compounds to quinones. The IR spectra of benzene and its derivatives show C-H valence vibrations around 3030 cm^{-1} and benzoid C=C valence vibrations at about 1500 cm^{-1} and 1600 cm^{-1}. For identification of substituted compounds, the range from 650 to 850 cm^{-1} (out-of-plane vibrations) is important. The UV spectra of benzene and its alkyl derivatives have three absorption bands at 180 nm, 200 nm and 255 nm ($\pi \rightarrow \pi^*$ transition). For many fused rings (especially linear fusions), the longest-wave absorption maximum is shifted into the visible range. Introduction of certain substituents, such as nitro or nitroso groups, also produces bathochromic shifts. In the ^1H NMR spectrum, the proton signals appear between 6.5 and 8.5 ppm; the ring current withdraws shielding from the protons. The coupling constants give important clues to the positions of substituents: J_{ortho} = 6 to 10 Hz, J_{meta} = 1 to 3 Hz, and J_{para} = 0 to 1 Hz. The mass spectrum of benzene or one of its derivatives has a strong molecular peak. The basis peak of an alkyl benzene is formed from the tropylium ion $C_7H_7^+$ (M = 91); some other typical fragments appear at M = 77, 65, 53, 51, 50 and 39.

Occurrence and extraction. Benzene and many of its homologs are found in petroleum from various sources, coke gas and coal tar, and they are extracted from these sources on an industrial scale. To meet the increasing demand for these hydrocarbons, aliphatic and saturated cyclic components of petroleum are now converted to A. by dehydrocyclization, dehydroisomerization, dehydrogenation or high-temperature cracking. Many polycyclic A. are found, in considerable quantities, in coal tar or the tars resulting from pyrolysis of gasoline or kerosene, and they are extracted from these sources. In addition, there are many synthetic methods, some of which are carried out industrially or in the laboratory.

1) Alkylbenzenes are synthesized from halobenzenes and haloalkanes by the Wurzt-Fittig reaction, using sodium; from A., haloalkanes and aluminum chloride by the Friedel-Crafts reaction; or from arylmagnesium chloride and haloalkanes by the Wurzt-Grignard reaction. With the versatile Friedel-Crafts acylations, the industrially available alkenes ethene and propene are often used instead of the haloalkanes as alkylation reagents.

2) Diphenylmethane and triphenylmethane are also accessible through Friedel-Crafts reactions, for example by reaction of benzene with benzyl halide, or of benzene with chloroform.

3) Fused A. can be obtained on a preparative scale by Friedel-Crafts acylation, for example naphthalene from benzene and succinic anhydride, or anthracene from benzene and phthalic anhydride.

Applications. Benzene and its homologs, especially toluene and the xylenes, are used as organic solvents, although their toxicity must be kept in mind (see Benzene). Methylbenzenes are converted to aromatic carboxylic acids by oxidation; alkyl-substituted cyclohexanes are obtained by hydrogenation. Fused A. are oxidized to quinones or carboxylic acids, depending on their structures. Hydrogenation can be carried out on selected rings or it may be total, producing other solvents or intermediates. Many aromatic functional compounds, which serve as intermediates in the synthesis of dyes, drugs, optical brighteners, laboratory and fine chemicals and explosives, are produced by electrophilic substitution of A. and subsequent reactions. Thus nitro compounds can easily be reduced to amines (see Aniline), sulfonic acids can be converted to phenols, and haloarenes can be further reacted with Grignard compounds. Halogenation of alkyl groups on A. to mono-, di- or trichloro compounds is also important; these compounds are converted by hydrolysis to alcohols, aldehydes or carboxylic acids. A. thus provide access to almost all functional compounds.

Arene complexes: see Organo-element compounds.

Arene diazonium salts: aromatic diazonium salts with the general formula $R\text{-}\dot{N}{\equiv}N|X^-$, where R is an aromatic or heteroaromatic group and X^- is a negative ion. Unlike aliphatic diazonium salts, A. are relatively stable, crystalline compounds which can be isolated, due to resonance stabilization of the charge. They tend to detonate when heated; the nitrates and perchlorates are especially dangerous. With the exception of the tetrafluoroborates, A. are readily soluble in water. They can be synthesized by Diazotization (see). A distinction is made between reactions in which the diazo group is displaced from the molecule in the form of nitrogen (see Diazo cleavage) and those yielding other nitrogen compounds, such as those leading to phenylhydrazine, phenylazide and the industrially important azo dyes (see Azo coupling).

Arene oxides: see Benzene oxide.

Arene thiols: same as Thiophenols (see).

Arene sulfonic acids: see Sulfonic acids.

Arg: abb. for arginine.

Arge high capacity process: see Fischer-Tropsch synthesis.

Argentan®: see New silver.

Argentometry: the most important method of precipitation analysis in which silver ions are the titrator. These form insoluble precipitates with halide and pseudohalide ions. The standard solution can be easily prepared from silver nitrate, a titration standard, but they are sensitive to light and should be stored in brown bottles.

There are several methods for recognizing the endpoint in A. The oldest is the ***Gay-Lussac method***, in which there is no indicator. If the titration is done with silver nitrate solution, the silver halide at first precipitates as a colloid. At the equivalence point, the precipitate clumps together and the solution becomes completely clear. This method can also be used in the reverse process in which the halide ions are used as titrator to determine silver concentration.

The ***Mohr method*** uses chromate ions as indicator at a pH of 5.5 to 8.0. A dark brown precipitate of silver chromate forms only after complete precipitation of silver chloride or bromide, and thus indicates the endpoint of the titration.

The ***Fajans method*** makes use of absorption indicators. Such indicators, e.g. fluorescein, dichlorofluorescein or eosin, are adsorbed on the surface of the silver halide precipitate after the equivalence point has been reached, and change their color. High salt concentrations in the sample solution interfere with this method, because they affect the adsorption of the indicator.

The ***Volhard method*** is suitable only for indirect titrations. After addition of an excess of silver nitrate standard solution, a thiocyanate standard solution is used for back titration. Iron(III), which forms a dark red complex with thiocyanate, is used as indicator.

The endpoint in A. can also be determined by electrochemical methods, which are sensitive enough to permit simultaneous determination of several halide ions.

Argentum: see Silver.

Arginase: an enzyme which catalyses the hydrolysis of arginine to ornithine and urea. A. (*Mr* 118,000) consists of four subunits, each of which contains an Mn^{2+} ion.

Arginine, abb. ***Arg***: α-amino-δ-guanidinovaleric acid, the most basic of the proteogenic amino acids (formula and physical properties, see Amino acids, Table 1). A. is particularly abundant in protamines and histones. In free form, it is found in red algae, cucurbits and conifers. Industrially, A. is obtained almost exclusively from hydrolysis of gelatins. It was first isolated in 1885 from lupine seedlings by Schulze and Steiger.

Argon, symbol ***Ar***: chemical element of the zeroth or eighth main group of the periodic system of the elements, the Noble gases (see); *Z* 18, natural isotopes with mass numbers 36 (0.337%), 38 (0.063%) and 40 (99.600%). Atomic mass 39.948, valence 0, density 1.784 g l^{-1} at 0 °C, m.p. - 189.2 °C, b.p. - 185.7 °C, crit. temp. - 122.3 °C, crit. pressure 4.8 MPa.

Properties. A. is a colorless, odorless, tasteless monoatomic gas. At 0 °C, 52 ml A. dissolves in 1 l water.

A. forms a very unstable hydrate and a clathrate with hydroquinone, but true "valence" compounds of A. are not known.

Analysis. A. is most conveniently separated by gas chromatography, and detected spectroscopically.

Occurrence. A suitable starting material for industrial production of A. is the residual gas from ammonia synthesis. Because fresh, A.-containing nitrogen is continuously introduced into the circulation, and the nitrogen is removed in the form of ammonia, A. is enriched to concentrations of more than 10%. The gas mixture is liquefied and fractionated by low-temperature distillation, yielding A. at very high purity. Air can also be used as a source of A., but the proximity of the boiling points of A. and oxygen (O_2 boils at - 182.97 °C) make it necessary to use a very efficient rectifying column and chemical treatment is still required after distillation.

Applications. As a cheap inert gas produced in large quantities industrially, A. is being used increasingly as a protective gas for reactions of readily oxidized substances and as a rinsing gas to remove gases from metal melts. A. is used as a protective gas in electrowelding, especially of readily oxidized light metals (aluminum, magnesium) and metals with very high melting points (titanium, zirconium, tantalum, molybdenum, tungsten; A. arc method). It is also used to fill light bulbs.

Historical. A. was discovered by Ramsay and Rayleigh in 1894 as a component of air.

Arndt-Eistert synthesis: a sequence of reactions described in 1935 for lengthing carboxylic acid chains by one CH_2 unit by reaction of carboxylic acid chlorides with diazomethane. The first product is an α-diazoketone, which releases nitrogen when heated with silver or silver oxide; a ketene is formed via a ketocarbene:

$$R\text{–}CO\text{–}Cl + | \bar{C}H_2\text{–}\overset{+}{N}\equiv N | \longrightarrow$$

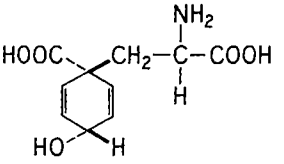
$$R\text{–}CO\text{–} | \bar{C}\text{–}\overset{+}{N}\equiv N | \xrightarrow{(Ag_2O)}$$

$$R\text{–}CO\text{–}\bar{C}H \longrightarrow R\text{–}CH{=}C{=}O \xrightarrow{+H_2O} R\text{–}CH_2COOH$$

The shift of the residue R with the bonding electron pair to the carbene carbon atom is known as the Wolff rearrangement (see). The reaction of water with the resulting ketene produces the corresponding carboxylic acid. If the diazoketone is decomposed in the presence of an alcohol or ammonia, the carboxylic acid ester or amide is formed directly.

Arnel®: a Synthetic fiber (see).

Arogenic acid: an aminocarboxylic acid discovered in 1974 as an intermediate in the biosynthesis of phenylalanine and tyrosine in prokaryotes (bacteria and blue-green "algae"), yeasts and green plants. It is formed by transamination of prephenic acid.

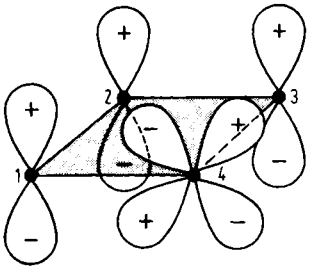


Aromatic: see Aromaticity.

Aromaticity: certain cyclic conjugated systems are more stable than the corresponding straight-chain compounds with the same number of π-electrons. The first theoretical explanation of A. was given by the Hückel method (see). From the HMO scheme for cyclic conjugated hydrocarbons, it can be seen that for systems with $4n+2$ π-electrons (n = 0, 1, 2...), there are very stable singlet states (*Hückel rule*). Conjugated ring hydrocarbons which obey the Hückel rule are called *aromatic*. Using the Hückel approximation, it can be calculated that cyclic conjugated systems are energetically more stable than linear conjugated systems. For example, the π-electron system of benzene (n = 1) has much lower energy than 1,3,5-hexatriene. In contrast to this, the π-electron systems of conjugated cyclic hydrocarbons with $4n$ π-electrons (n = 1, 2...) are less stable than the corresponding linear conjugated systems. This applies to cyclobutadiene, which has higher energy than 1,3-butadiene. Cyclic conjugated hydrocarbons with $4n$ π-electrons are therefore called *antiaromatic*.

If a $2p_z$ orbital is replaced by a 3d atomic orbital, for example in cyclobutadiene, the topology of the

bonds changes; there is a phase shift associated with a change in sign of an orbital lobe (Fig.). Such a system is called a *Möbius system*; it can occur, for example, in π-complexes of transition metals. In Möbius systems, in contrast to Hückel systems, even the lowest-energy molecular orbital is doubly degenerate. As a result, the aromaticity properties are reversed. Möbius-type cyclic conjugated systems are aromatic if they have $4n$ π-electrons (n = 1, 2 ...), while those with $4n+2$ π-electrons (n = 0, 1, 2...) are antiaromatic. Möbius systems are therefore also called *anti-Hückel systems*).



Möbius system (phase shift between atoms 1 and 4).

In general, the following rule applies to the topology of cyclic conjugated systems and their A.: if the π-atomic orbitals can be arranged in such a way that the number of minimal phase shifts is zero or even, the system is Hückel type (*Hückel topology*). If the number of phase shifts is odd, it is Möbius type (*Möbius topology*). Cyclic conjugated molecular ions (e.g. cyclopentadienyl anion) and heterocyclic conjugated systems (e.g. pyridine) can also be treated by this rule.

Arosolvane process: a process for obtaining aromatics by Extraction (see).

Aroxyls: term for aryl-substituted oxygen radicals of the phenoxyl type, C_6H_5O.

Arrhenius acid-base definition: see Acid-base concepts.

Arrhenius equation: in kinetics, an equation first suggested by S. Arrhenius (1869) which describes the temperature dependence of the rate constants of a very large number of reactions: $k = A \exp(-E_a/RT)$. k is the rate constant, R, the general gas constant and T the absolute temperature. The factor A (also called the *frequency factor* or *action constant*) and the *activation energy* E_0 are characteristic of each reaction, and must be determined experimentally. The A. can be derived theoretically from collision theory.

Arrow poisons: poisons (usually from plants) which are rapidly toxic or fatal when injected parenterally (through skin wounds). They are used for hunting and war by certain indigenous peoples. The best known P. are the African A. ***ouabain*** (chemically, g-strophanthin), a cardiac poison; the South American A. ***curare***, which paralyzes the voluntary muscles; and ***Javanese A.***, which contains either strychnine (a convulsant which acts primarily in the spinal cord) or antiarine (which has an effect similar to those of strophanthin and strichnine).

Arsane: same as Arsenic hydride (see).

Arsenates: salts of Arsenic acid (see).

Arsenic: (the poison) see Arsenic oxides.

Arsenic, symbol ***As***: chemical element from the fifth main group of the periodic system, the Nitrogen-phosphorus group (see). It is a semimetal, Z 33, with only one natural isotope, atomic mass 74.9216, valences III and V, standard electrode potential 0.2475 V ($As + 3\ H_2O \rightleftharpoons H_3AsO_3 + 3\ H^+ + 3e$).

Properties. A. exists in three modifications. The ***gray, metallic*** modification is thermodynamically stable at room temperature; its lattic consists of infinite layers in which the As atoms are linked in puckered, six-membered rings. It forms a steel-gray, brittle, rhombohedral crystal with a metallic sheen. Its Mohs hardness is 3 to 4, density 5.727, electrical conductivity 3.0 Sm mm^{-2} (at 20 °C). In a closed tube, it melts at 817 °C under its own vapor pressure of 2.8 MPa, and sublimes at 613 °C, forming a yellow vapor which consists of As_4 molecules. The proportion of As_2 molecules in the vapor increases as the temperature increases. If arsenic vapor is quenched, it condenses as waxy, ***yellow nonmetallic A.***, which is soluble in carbon disulfide. Its density is 2.064, and its cubic lattice is comparable to that of white phosphorus, in that it consists of As_4 molecules. Yellow A. is rapidly converted to the gray form, especially when exposed to light. If arsenic vapor is condensed on surfaces where the temperature is 100 to 200 °C, it forms the hard, brittle, black and shiny ***amorphous A.***. This form does not conduct electricity. In the presence of mercury, it is converted at 125-175 °C to the unstable orthorhombic ***black A.***, which has a structure analogous to that of black phosphorus.

A. burns in air > 180 °C to form arsenic(III) oxide, As_2O_3. It burns in chlorine to give arsenic(III) chloride, $AsCl_3$. Concentrated nitric acid or aqua regia oxidizes A. to arsenic acid: $As + 5\ HNO_3 \rightarrow 5\ NO_2 + H_3AsO_4 + H_2O$; in dilute nitric acid or concentrated sulfuric acid, A. is dissolved to form arsenous acid: $2\ As + 3\ H_2SO_4 \rightarrow 2\ H_2AsO_3 + 3\ SO_2$. A. forms alloys with many metals; most of these alloys are brittle.

> Pure arsenic is reported to be nontoxic. However, since it is readily oxidized in the air, and it is difficult to be sure no impurities are present, the element should be treated with caution.

Analysis. The Gutzeit test (see), Marsh test (see), Bettendorf test (see) or Berzelius test (see) can be used for qualitative analysis. In the systematic separation procedure, A. is precipitated as arsenic sulfide, separated by treatment with $(NH_4)_2S$, and its presence indicated by precipitation as ammonium magnesiumarsenate, $NH_4MgAsO_3 \cdot 6H_2O$. Iodometry or atomic absorption spectroscopy is used for quantitative determination of As^{3+}.

Occurrence. A. makes up $5.5 \cdot 10^{-4}$% of the earth's crust. It is occasionally found in the elemental state in nature, but it is more commonly found as arsenides, arsenic sulfides and arsenic oxides. Some important minerals are arsenopyrite, FeAsS, loellingite, $FeAs_2$, cobaltine (cobalt glance), CoAsS, gersdorffite (arsenic nickel glance), NiAsS, realgar, As_4S_4 and

oripiment, As_2S_3. Claudetite or arsenolite, As_2O_3, are weathering products of arsenic ores. A. occurs very widely; it can always be detected in the soil and in plant and animal tissues.

Extraction. If arsenopyrite is heated in the absence of air, elemental As forms and sublimes off: $FeAsS \rightarrow FeS + As$. However, the element is usually produced industrially from arsenic-containing byproducts of various metallurgical processes. These are worked up to arsenic(III) oxide, As_2O_3, and reduced to As with carbon. For the production of very pure As, the oxide can be reduced with hydrogen.

Applications. Very pure A. is used to dope silicon and germanium semiconductors, and in the production of gallium arsenide. Most of the As produced is used in alloys, especially of lead and copper. For example, the lead-antimony-arsenic alloy used as the lattice in lead batteries contains 0.5% As.

Historical. A few arsenic compounds were known in antiquity. Production of the elemental form was first described by Albertus Magnus about 1250.

Arsenic acid: H_3AsO_4, has been isolated only as the semihydrate, $H_3AsO_4 \cdot 1/2H_2O$, colorless, hygroscopic crystals; M_r 150.95, m.p. 35.5 °C. In aqueous solution, A. is a medium strong triprotic acid: $pK_1 = 2.32$, $pK_2 = 7$, $pK_3 = 13$. There are three series of salts derived from A., the primary arsenates or dihydrogenarsenates, $M^IH_2AsO_4$, the secondary or hydrogenarsenates $M^I_2HAsO_4$ and the tertiary arsenates $M^I_3AsO_4$. Overall, A. and the arsenates are very similar in their chemistry to phosphoric acid and the phosphates. For example, A. forms a relatively insoluble, colorless ammonium magnesium arsenate, $NH_4MgAsO_4 \cdot 6H_2O$ and an insoluble, chocolate-brown silver arsenate, Ag_3AsO_4. Like the phosphoric acids, A. can be a component of heteropolyacids. For example, in nitric acid solution, ammonium molybdate and A. form the relatively insoluble yellow ammonium dodecamolybdatoarsenate $(NH_4)_3[As(Mo_{12}O_{40})]$. All the above precipitations can also be used as detection reactions for arsenic or arsenates. In contrast to phosphoric acid, A. is a strong oxidizing agent; for example, it can oxidize iodide to iodine. A. is obtained by oxidation of arsenic or arsenic(III) oxide with conc. nitric acid.

Arsenic(III) chloride, ***arsenic trichloride***: $AsCl_3$, a colorless, oily and very poisonous liquid which fumes in moist air; M_r 181.28, density 2.163, m.p. - 8.5 °C, b.p. 130.2 °C. A. is obtained by burning arsenic in a chlorine atmosphere, or by reaction of arsenic(III) oxide, As_2O_3 with dry hydrogen chloride at 180-200 °C. The reaction of aqueous hydrochloric acid with As_2O_3 leads to an equilibrium: $H_3AsO_3 + 3\,HCl \rightleftarrows AsCl_3 + 3\,H_2O$; in the presence of a large excess of HCl, this equilibrium is shifted to the right. By distilling off the water, it is possible to convert As_2O_3 completely to $AsCl_3$. A. is an important starting material in the preparation of various arsenic compounds, especially organic ones.

Arsenic hydride, ***arsine, arsane***: AsH_3, a colorless and very poisonous gas with an unpleasant, garlic-like odor; M_r 77.95, m.p. - 116.3 °C, b.p. - 55 °C. A. burns in air with a pale blue flame to give arsenic(III) oxide and water: $2\,AsH_3 + 3\,O_2 \rightarrow As_2O_3 + 3\,H_2O$. However, if a cold object is held in the flame, the combustion is not complete and a black arsenic mirror precipitates: $4\,AsH_3 + 2\,O_2 \rightarrow 4\,As + 6\,H_2O$. When heated, A. decomposes into arsenic and hydrogen. The last two reactions are used in the Marsh test (see). A. is a strong reducing agent, which is able, for example, to reduce silver cations to metallic silver. It reacts with solid silver nitrate to form the double salt $Ag_3As \cdot 3AgNO_3$ (see Gutzeit test). A. is formed in the reaction of nascent hydrogen with arsenic or arsenic compounds. It is used as a dopant in the semiconductor industry.

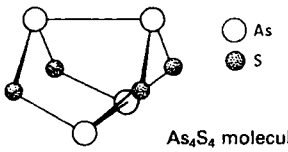
Arsenic oxides: ***Arsenic(III) oxide, arsenic trioxide, arsenic***; M_r 197.84, exists in two modifications. The cubic modification is stable at room temperature, has density 3.865, sublimes 193 °C, and is converted at 221 °C to a monoclinic form, density 4.15, b.p. 457.2 °C. As_2O_3 is obtained by combustion of arsenic; it exists either as an amorphous, colorless powder, density 3.738, m.p. in a closed tube, 312.3 °C, or as a glassy mass. The lattice of the cubic modification and the vapor consist of As_4O_6 tetrahedra, which are structurally comparable to those of phosphorus(III) oxide (see Phosphorus oxides). In the monoclinic and glassy forms, $[AsO_3]$ pyramids are joined by oxygen atoms to infinite layers. As the temperature increases, the tetrahedra in the vapor phase dissociate to As_2O_3 units. As_2O_3 is not very soluble in water. It is amphoteric with respect to acids and bases. In alkali hydroxide solutions, it dissolves to form arsenites (see Arsenous acid), while it comes to an equilibrium with hydrochloric acid: $H_3AsO_3 + 3\,HCl \rightleftarrows AsCl_3 + 3\,H_2O$. When heated with carbon, hydrogen or sodium cyanide, As_2O_3 is reduced completely to arsenic.

> Arsenic(III) oxide and arsenites are strong poisons. The lethal dose for a human being is approximately 0.1 g As_2O_3. It is absorbed from the gastrointestinal tract, and to a lesser extent through the skin as well. Dust is also absorbed in the lungs. The individual sensitivities to As_2O_3 vary widely. By consuming gradually increasing amounts, a person can become habituated (arsenic eaters), so that significantly larger doses can be tolerated without severe damage. The symptoms of acute poisoning are pains in the body, vomiting, diarrhea, dryness in the mouth and throat, convulsions, drop in blood pressure, etc., leading to paralysis and death.

As_2O_3 is found in nature as cubic arsenolite and monoclinic claudetite. It is obtained industrially by roasting of arsenopyrite according to the equation: $2\,FeAsS + 5\,O_2 \rightarrow Fe_2O_3 + 2\,SO_2 + As_2O_3$. The oxide sublimes off. As_2O_3 was formerly used in medicine. Now it is used as a rodenticide, to preserve furs, bird skins and hides, and is the starting material for synthesis of various arsenic compounds, especially organic ones.

Arsenic(V) oxide, arsenic pentoxide: As_2O_5, colorless amorphous powder or glassy mass; M_r 229.84, density 4.32, dec. 315 °C. As_2O_5 dissolves in water, forming arsenic acid, H_3AsO_4. It decomposes when heated, forming As_2O_3 and oxygen. It is obtained by dehydration of arsenic acid.

Arsenic sulfides: ***Arsenic monosulfide***, $(AsS)_4$, ruby-red crystals or an amorphous mass; M_r 427.94. The monoclinic lattice consists of As_4S_4 molecules, the structure of which is derived from that of As_4 tetrahedra by insertion of sulfur in four As-As bonds (Fig.). As_4S_4 occurs in nature as realgar; it is synthesized by fusion of equimolar amounts of elemental sulfur and arsenic, or by heating arsenopyrite with pyrite: $4\ FeAsS + 4\ FeS_2 \rightarrow 8\ FeS + As_4S_4$. It is used to remove hair from hides which are to be tanned.



As_4S_4 molecule

Arsenic(III) sulfide, arsenic trisulfide, As_2S_3. A lemon-yellow, monoclinic crystalline powder; M_r 246.04, density 3.43, m.p. 300 °C, b.p. 707 °C. The compound is insoluble in water and acids (pK_s = 25.3) and is obtained by precipitation of As^{3+} ions with hydrogen sulfide. Crystalline As_2S_3 has a layered structure comparable to that of monoclinic arsenic(III) oxide, and the vapor phase consists of As_4S_6 molecules which correspond structurally to those of P_4O_6 or As_4O_6. As_2O_3 dissolves in ammonium sulfide solution to form thioarsenites according to the equation $As_2S_3 + 3\ S^{2-} \rightarrow 2\ AsS_4^{3-}$. As_2S_3 occurs in nature as oripiment. The pure compound is not poisonous, because of its insolubility, and is used as a pigment in paints.

Arsenic(V) sulfide, arsenic pentasulfide, As_2S_5, is a yellow, amorphous powder; M_r 310.16. As_2S_5 is insoluble in water and acids, but dissolves in ammonium sulfide to form thioarsenates. It is made by passing hydrogen sulfide through a very acidic solution of arsenic acid, or by fusion of As_2S_3 and sulfur.

Arsenides: compounds of arsene with metals. A. are formed by fusion of the elements. The alkali and alkaline earth arsenides, and zinc arsenides, are derived from arsenic hydride, AsH_3, and should be considered its salts. They are decomposed by water with generation of AsH_3. The heavy metal A. often have complicated stoichiometries and are considered intermetallic phases. Gallium arsenide, GaAs, and indium arsenide, InAs, are important in semiconductor technology.

Arsenites: the salts of Arsenous acid (see).

Arsenous acid, ***arsenic(III) acid***: H_3AsO_3, a very weak, triprotic acid (pK_1 = 9.22) which cannot be isolated. The dilute aqueous solution of A. is obtained by dissolving its anhydride, arsenic(III) oxide, in water. Its salts, the poisonous *arsenites* or *arsenates(III)*, are derived either from the ortho form of A. or from the meta form, $HAsO_2$. There are three types of ortho-form derivatives: $M^IH_2AsO_3$, $M^I_2HAsO_3$ and $M^I_3AsO_3$. The meta-form derivatives have the formula M^IAsO_2, and contain polyanions. In strong hydrochloric acid, A. is in equilibrium with arsenic(III) chloride: $H_3AsO_3 + 3\ HCl \rightleftharpoons AsCl_3 + 3\ H_2O$. Elemental arsenic is precipitated from this solution by tin(II) chloride. On the other hand, arsenites or A. are oxidized by iodine in neutral solution to arsenates: $H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2\ H^+ + 2\ I^-$. In acid solution, the reaction reverses.

Arsine: same as Arsenic hydride (see).

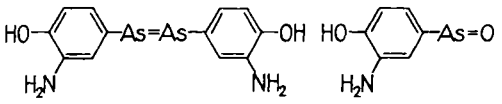
Arsines: see Organoarsenic compounds.

Arsinic acids: see Organoarsenic compounds.

Arsonium salts: see Organoarsenic compounds.

Arsonic acids: see Organoarsenic compounds.

Arsphenamine, ***Salvarsan®***: an organic arsenic compound with which it was possible, for the first time, to heal syphilis with a chemical pharmaceutical. A. is usually shown as an arseno compound (-As=As-), but it may be a trimer with a ring of 6 As atoms. The active form of A. is oxophenarsine.



Arsphenamine Oxophenarsine

Because of its high toxicity, A. is no longer used. It was developed in 1909 by P. Ehrlich.

Aryl-, abb. ***Ar-***: a term for a group derived from an arene by removal of one of the hydrogen atoms on the aromatic ring, e.g. phenyl- or naphthyl. Aryl groups are important in the systematic nomenclature of aromatic compounds. Aryl radicals are unstable and very short-lived, as are the corresponding carbenium ions.

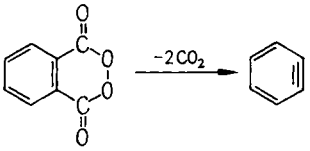
Arylation: introduction of an aryl group into an organic compound. An important example is the addition of aryl radicals to unsaturated compounds. The radicals can be generated photochemically from halogen-substituted arenes or diazonium salts.

Aryl halides: same as Haloarenes (see).

Aryloxyalkanoic acid herbicides: same as Growth-hormone herbicides.

Arylsulfatases: see Esterases.

Arynes: aromatic ring systems with a formal triple bond in the aryne ring. The simplest compound of this type is *1,2-dehydrobenzene (benzyne)*. A. are short-lived, very reactive intermediates which can be generated and detected by UV spectroscopy at - 265 °C:



Actually, the structure of these compounds is best represented by the lowest-energy singlet state.

As: symbol for arsenic.

Asant: see Gum resins.

Asbestos: fibrous, silicate minerals with varying compositions. There are two groups, ***serpentine A.*** and ***amphibol*** or ***hornblende A.***. Serpentine A. include chrysotile A., $Mg[(OH)_8/Si_4O_{10}]$, which is very resistant to heat (m.p. 1500 °C), but not to acids. The most important of the hornblende A. is crocydolite, a sodium iron silicate, which is less resistant to heat (m.p. 1150 °C). About 90% of the A. used as a heat-resistant material is chrysotile A., and only about 5%

is crocydolite. Because of its carcinogenicity (bronchial carcinomas from asbestos dust), A. is being replaced in many applications by heat-resistant mineral and glass fibers. The world production reached a maximum in 1975 of about 5.5 million tons. Crocydolite is more carcinogenic than chrysotile A.. The mineral mixture talcum can contain up to 50% asbestos.

Ascaridol: 1,4-peroxo-*p*-menth-2-ene, a monoterpene found in the oil of American wormseed (*Chenopodium ambrosiodes* var. *anthelminticum*). The oil was formerly used as an drug against intestinal worms (ascarides, hookworms). However, it has severe side effects.

Ascarite: sodium hydroxide adsorbed to asbestos. A. is used to absorb carbon dioxide, forming sodium carbonate and water. It is used in elemental analysis and for gravimetric determination of carbon.

Ascorbic acid: same as Vitamin C (see).

Ashes: the inorganic residue remaining after complete combustion of plant or animal substances. ***Plant A.*** contain water-soluble potassium and sodium carbonates, sulfates and chlorides, as well as insoluble calcium, magnesium and iron carbonates, phosphates and silicates. ***Coal A.*** contain mainly clay, iron oxide and sulfates or silicates. They therefore are of no use as fertilizers. ***Bone A.*** consist essentially of calcium phosphate and can be used as fertilizer.

ASIS effect (for Aromatic Solvent Induced Shift), the shift in an NMR signal caused by transferring the substance from a nonpolar (e.g. deuterochloroform, $CDCl_3$) to an aromatic (e.g. benzene) solvent. The A. is often used to elucidate stereochemical problems. Benzene, for example, forms collision complexes with dissolved polar molecules; on the time average, these prefer certain spatial orientations. The chemical shifts (see NMR spectroscopy) of the individual nuclei of the dissolved molecule are affected differently, depending on their spatial relationship to the aromatic ring. The solvent shift $\delta = \delta_{CDCl_3} - \delta_{C_6H_6}$ for individual nuclei gives essential information on the structure of the dissolved compound (e.g. about its conformation). The ASIS has been particularly useful in the steric assignment of ketones.

Asn: abb. for Asparagine.

Asp: abb. for Aspartic acid.

Asparagine, abb. ***Asn***: the β-semiamide of aspartic acid, and a proteogenic amino acid (formula and physical properties, see Amino acids, Table 1). As a component of proteins, A. occurs widely in nature, and is found in free form in the sprouting seeds of many plants. It was the first proteogenic amino acid discovered; it was isolated from asparagus (*Asparagus officinalis*) in 1806 by Robiquet.

Aspartame, ***L-asparagyl-L-phenylalanine methyl ester***: H-Asp-Phe-OMe, a synthetic sweetener about two hundred times sweeter than sucrose. A. was discovered accidentally in 1969 during recrystallization of a peptide intermediate. Various methods have been developed for its commercial synthesis, including a protease-catalysed synthesis.

Aspartase: a lyase found in microorganisms and higher plants which cleaves aspartic acid to fumaric acid and ammonia. The reverse reaction is used commercially: A. or microorganisms with high A. activity are used to synthesize aspartic acid from fumaric acid and ammonia on an industrial scale.

Aspartic acid, abb. ***Asp***, ***α-aminosuccinic acid***: $HOOC\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH$, a proteogenic amino acid found in many plant and animal proteins. In the presence of aminotransferases, A. is reversibly coverted to oxaloacetic acid, an important member of the citric acid cycle. Thus protein and carbohydrate metabolisms are linked through A. DL-A. is synthesized industrially by addition of ammonia to maleic or fumaric acid under high pressure. However, the enzymatically catalysed addition of ammonia to fumaric acid, in which yields of 90% L-A. are obtained, is also economically important.

Asphalt: natural or artificial mixture of bitumen with minerals. A. is dark brown to black, solid, usually not very hard, with either a matte surface or a pitch-like shine. It sheds water and is resistant to alkalies and dilute mineral acids, but is soluble in organic solvents such as benzene, gasoline, chloroform and carbon disulfide. When heated, A. becomes soft or liquid. Asphaltenes, asphalt acids, etc. can be extracted from A., which have widely varying compositions. Natural A. cover the entire range from mineral-free bitumen to bituminous rocks containing relatively little bitumen.

1) ***Natural A.*** is probably an oxidation and polymerization product of petroleum produced by the action of microorganisms. It is found in large deposits. *Asphaltite* is a hard natural A. with less than 30% oil content, found in Utah and West Virginia in the USA. *Asphalt rocks* (less than 10% bitumen) are found on Trinidad, in the USA, the Andes and Albania. *A. limestones* are found in West Germany, France, Switzerland and Italy. *A. sand* (3 to 24% bitumen) is found in the USA, Canada, Spain, the USSR, Rumania and Bulgaria. *Lake A.*, found on Trinidad, contains 39% bitumen, 30% mineral components and 31% emulsified lake water. *A. shale* is found in West Germany.

2) ***Artificial A.*** *Petroleum A.* are residues left after distillation of crude oil or its A.-rich distillates; it is black and rigid at normal temperatures. *Chemical A.* (*acid A.*, *blast A.*) are products which accumulate in many processes and from various organic raw materials, especially mineral and resin oils, tars, resins, waxes and natural A. through the action of various chemicals.

Applications. The greatest use for A. is in making roads. ***Cold A.*** is an emulsion of bitumen and water, stabilized by emulsifiers. Cold A. is used to spray onto gravel on roadbeds; the emulsion is broken and the gravel is stuck together. Cold A. is also used as a protective paint.

A solution of A. in benzene or turpentine oil is ***A. paint***, which is used to cover metal surfaces in galvanizing and etching processing, and as a rust protection.

Aspidosperma alkaloids: see Alkaloids, Table.

Aspirin: see Acetosalicylic acid.

Association colloids: see Colloids.

Astatine, symbol ***At***: a radioactive, very short-lived element from the 7th main group of the periodic system, the Halogens (see). At is a nonmetal, *Z* 85, with isotopes with mass numbers 196 to 219 (two nuclear isomers each for the mass numbers 198, 200, 202 and 212). The atomic mass of the most stable isotope is 210 ($t_{1/2}$), which decays by K-capture (99.83%) or

α-emission (0.17%). The element has valences -1, +1, +5 and +7, m.p. ≈ 300 °C, b.p. ≈ 370 °C, standard electrode potential (At^-/At_2) is +0.25 V.

The isotopes ^{215}At, ^{218}At and ^{219}At have very short half-lives: ^{215}At, $t_{1/2}$ $1.64 \cdot 10^{-4}$ s, α-emission; ^{218}At, 1.3 s, 99.9% α-emission and 0.1% β-emission; and ^{219}At, 0.9 min, 97% α and 3% β emission. These are members of the natural decay series initiated by β-decay of polonium or α-decay of francium, and are therefore found in extremely small amounts in the earth's crust. (The At content of the lithosphere is estimated to be about 70 mg.)

The relatively stable isotopes with mass numbers 209 to 211 have half-lives between 5.5 and 8.1 h. They are formed by irradiation of bismuth 209 with 30-50 Mev α-particles, e.g. according to $^{209}Bi + {}^4He \rightarrow {}^{211}At + 2\,{}^1n$. They are also found as spallation products from irradiation of thorium or uranium with very energetic protons. These isotopes are separated from their mixtures by wet chemistry or gas thermochromatography. A. is less volatile than iodine. It is readily soluble in organic solvents and forms interhalogen compounds such as AtCl, AtBr and AtI with other halogens. At is reduced by strong reducing agents to At^-; ***astatine hydride***, HAt, is a stronger reducing agent than hydrogen iodide, HI. Mild oxidizing agents, such as Fe^{3+} or Br_2, convert At to the level of ***hypoastatous acid***, HAtO. Strong oxidizing agents like peroxodisulfate oxidize A. to ***astatate(V)***, $[AtO_3]^-$, while xenon difluoride in hot, alkaline solution oxidizes At^- to ***perastatate, astatate(VII)***, $[AtO_4]^-$. Many ***organoastatine compounds***, e.g. C_2H_5At, C_6H_5At, C_6H_4AtX (X = Cl, Br, I) and $AtCH_2COOH$, have been synthesized.

Historical. The possibility that iodine had a heavier homolog (eka-iodine) was predicted by Mendeleyev. Corson, McKenzie and Segrè discovered A. in bismuth which had been irradiated with 20-MeV α-particles. It was only later shown that extremely small amounts of At ($\approx 3 \cdot 10^{-24}$% of the earth's crust) exist in nature, in uranium and thorium minerals. The name A. comes from the Greek "astatos" = "unstable".

Astatine emanation: see Radon.

Aston's isotope rule: see Isotopes.

Astraphloxin FF: see Polymethane pigments.

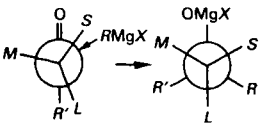
Astrazone red, GB: see Polymethane pigments.

asymm-: see Nomenclature, sect. III D.

Asymmetric: see Nomenclature, sect. III D.

Asymmetric carbon atom: see Stereoisomerism.

Asymmetric synthesis: synthesis of unequal amounts of the enantiomers of a chiral molecule (see Stereoisomerism, 1.1), starting from an achiral compound. Since not all chiral compounds are asymmetric, it is better to call this process ***stereoselective synthesis***. 1) ***Absolutely stereoselective syntheses*** are those in which the optically active compound is made from the non-active starting material without the help of an optically active reagent, simply through the effects of chiral physical processes, such as circularly polarized light or the enantiomorphic crystal structure of one of the reactants. The optical yield is only a few percent. 2) ***Diastereoselective syntheses (internally asymmetric syntheses)***. A new center of chirality is formed in the reaction of a molecule with a *diastereotypic group* or *side* (see Topic groups); the original chirality center influences the formation of the new one. This type of diastereoselective synthesis is seen, for example, in the reaction of carbonyl compounds which have chirality centers adjacent to the carbonyl with Grignard reagents. These obey *Cram's rule*: if the carbonyl compound tends to be in the conformation in which the C=O group is flanked by the two smaller groups of the adjacent chirality center, the reagent attacks preferentially from the side of the smallest ligand, and selectively forms the corresponding diastereomer (Fig.).



Reaction according to Cram's rule. *S*, small; *M*, medium; *L*, large.

3) ***Enantioselective syntheses (external asymmetric syntheses)***. Optically active compounds are made from compounds containing enantiotopic groups or sides (true achiral substances) by means of a chiral reagent or catalyst.

Asymmetry effect: see Debye-Hückel theory.

At: symbol for astatine.

Atactic: see Polymers.

Ataractica: see Psychopharmaceuticals.

At. U.: abb. for Atomic units (obsolete).

Atebrin®: see Mepacrine.

Atmospherilics: air pollutants which stimulate Corrosion (see) through the atmosphere. Sulfur dioxide, chloride, particulates and atmospheric moisture all play a part in corrosion.

Atmungsferment: see Cytochrome oxidase.

Atom: the smallest electrically neutral particle of a chemical element, which cannot be further divided by chemical means. The properties of the A. determine the chemical and physical properties of the element. A. can be subdivided by physical means, and in this way they have been observed to consist of positively charged ***nuclei*** and negatively charged ***electrons*** which form a cloud around the nucleus (see Atom, models of). If electrons are removed or added, the particle is called a positive or negative ion, respectively.

The nucleus contains protons and, in all cases but one (^1H), neutrons. The ratio of neutron number to proton number increases from 1.0 in ^4He to higher values in heavier elements. The nucleons (protons and neutrons) make up nearly the total mass of the A., and the number of nucleons is equal to the *mass number M* of the A. (see Atomic mass). A. with the same atomic number (number of protons) can have different numbers of neutrons. These atoms have nearly identical chemical behavior, and are called Isotopes (see) of the element.

The relative size of an A. is the Atomic radius (see). The positions of A. in crystal lattices have been determined by x-ray, electron and neutron beam interference (see X-ray structure analysis). An atomic model is a conceptual image of the structure of an A.

Atomic absorption spectroscopy, abb. ***AAS***: methods of Atomic spectroscopy (see) for determination of single elements, especially of inorganic traces and minor components.

Principle. A. utilizes the absorption of single atoms for quantitative determination of their amounts. The free atoms are usually obtained from solutions by thermal evaporation and dissociation in an absorption chamber. This chamber is irradiated by light from a special source; the change in intensity of the chosen spectral line (the extinction) is proportional to the number of atoms present in the chamber, and thus to their concentration in the solution.

Fig. 1. is a diagram of an atomic absorption spectrometer. Free atoms are generated in the atomizer, a process which requires energy. This is provided by chemical processes (flames) or electric resistance heating (graphite or quartz atomizers). In the first case, the dissolved sample is sprayed into the flame as an aerosol. Combustion of ethyne/air mixtures yields temperatures up to 2500 K, while mixtures of ethyne/NO_2 produce flame temperatures of 3100 to 3200 K; these are available for samples which are less readily volatilized.

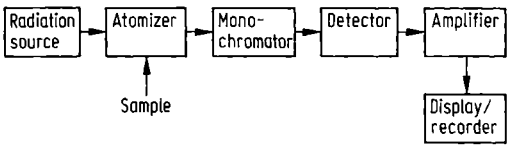


Fig. 1. Diagram of an atomic absorption spectrometer.

Flameless A. is also widely used, usually with electrothermal atomization of the sample in a graphite cuvette. A solution of the sample is usually injected into the cuvette by micropipette, and very rapidly heated to 2000 to 3000 K by means of a resistance heater. The sample is dried, incinerated and finally atomized.

In neither method is the temperature of the Plasma (see) high enough to excite the free atoms to electronic states above the ground state (the table shows the ratio of the number N of excited atoms to the number N_0 in the ground state for various elements and temperatures, calculated from the Maxwell-Boltzmann distribution (see). There are three advantages of A. which result from this fact. 1) Since the observed absorption processes start from the ground state, they are of high intensity, and this is the basis of the high analytical sensitivity of the method. 2) Since only those absorption lines are observed which start from the ground state, the spectra have relatively few lines, and there is thus little overlapping of spectral lines from different elements. As a result, the method is highly selective. 3) Since the fraction of atoms in the ground state at these temperatures is very high, it can be taken as approximately constant. As a result, the absorption process is largely independent of temperature, in contrast to the emission process.

Only some solids can be studied. Special methods, such as vaporization of microamounts of solids with laser beams, can be used to examine solids which cannot be readily vaporized from solution.

Ratio N/N_0 for the resonance lines of a few elements

Resonance line		Temperature in K			
		2000	3000	4000	5000
Na	589.0 nm	$9.86 \cdot 10^{-6}$	$5.88 \cdot 10^{-4}$	$4.44 \cdot 10^{-3}$	$1.51 \cdot 10^{-2}$
Ca	422.7 nm	$1.21 \cdot 10^{-7}$	$3.69 \cdot 10^{-5}$	$6.03 \cdot 10^{-4}$	$3.33 \cdot 10^{-3}$
Zn	213.9 nm	$7.29 \cdot 10^{-5}$	$5.58 \cdot 10^{-10}$	$1.48 \cdot 10^{-7}$	$4.32 \cdot 10^{-6}$

The *light sources* used in A. are chosen to have narrow linewidths and high spectral intensity. Hollow-cathode lamps fulfill these requirements. These lamps consist of a glass tube filled with a noble gas at 250 to 500 Pa; the cathode is made of the same element as is to be detected (Fig. 2). A separate lamp is required for each element. When a voltage is applied, there is a glow discharge in the lamp. Both the noble gas and the metal vapor emit their characteristic spectra; by reduction of the collision and Doppler spreading (see Linewidth), the emitted lines can be made very narrow, even narrower than the corresponding absorption lines (Fig. 3).

Fig. 2. Hollow cathode lamp

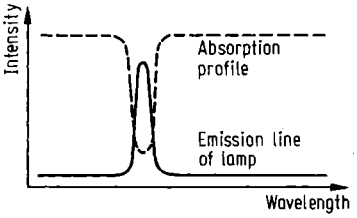


Fig. 3. Linewidths of emission and absorption lines.

This improvement was introduced by Walsh in 1955; it insures that all the incident radiation can be absorbed, and this leads to a great improvement in the sensitivity of the method.

Another type of light source is an electrodeless discharge lamp, in which excitation is achieved by inductive coupling with the high-frequency energy of a transmitter.

The absorption process is described by an equation analogous to the Lambert-Beer law (see): $E = \log I_0/I_D = k'N$, where E is the extinction, N is the number of absorbing particles, and k' is a constant.

Since the radiation from the radiation source contains several spectral lines, a *monochromator* is used to remove all but one line. As a rule, the resonance line corresponding to the transition from the ground state to the first excited state of the element is used for its determination. Since the most important absorption lines of most elements are in the UV, the optical elements must be made of quartz. The intensity of the incident and transmitted light is measured by a Secondary electron multiplier (see) used as the *detector*. It is placed at the exit slit of the mono-

chromator, and converts the light signal into an electric signal which is amplified and displayed.

Atomic absorption spectrometers can be built either as single or as double-beam devices (see Spectral instruments). Single-beam instruments require stability in the emission from the light source, but intensity fluctuations do not affect double-beam measurements. To eliminate interfering emissions of flames and atomizers, the radiation from the hollow-cathode lamps is usually modulated.

The results are evaluated either by use of a calibration curve, in which the measured extinctions E of various standards are plotted against their concentrations c, or by an addition method. If properly prepared, the calibration curve gives more precise and more accurate results. The addition method is more rapid, but often produces systematic errors. The accuracy of the results can be affected by Matrix effects (see). In the case of A., these are most often factors which affect the vaporization and dissociation of the sample. Efforts should be made to eliminate them, for example by addition of substances which bind the interfering matrix, or changing the temperature of the flame.

Applications of A. In the past 25 years, A. has become the most important method of analysis for determination of traces of inorganic substances in solutions. Using A., about 70 of the elements can be determined, mostly metals and semimetals. Determination of nonmetals is often difficult, because the resonance lines of these elements are usually below 200 nm, and because some of them form stable molecules which do not dissociate readily. A. can be used to analyse both micro- and macrosamples. Electrothermal atomization in graphite cuvettes is especially useful for microsamples. This is because there are no losses of solution through ashing of the sample in the flame, and all of the sample is vaporized essentially simultaneously. Use of solutions requires that the sample be dissolved.

The applications of A. are extremely varied. It is used in any situation where inorganic components, especially metals, are analysed. This is the case in numerous areas of science, medicine and technology, including biochemistry, toxicology, environmental protection, food analysis, agriculture and metallurgy.

Atomic bond: see Chemical bond.

Atomic emission spectroscopy, abb. ***AES***: methods of atomic spectroscopy used for qualitative and quantitative determination of elements in solid and liquid samples. The sample is converted to the plasma state by an excitation source (e.g. flame, arc, spark or high frequency electromagnetic radiation). The light emitted by the plasma is focused on the entrance slit of a monochromator, spectrally resolved and allowed to impinge on a photographic plate (spectrograph) or photoelectric detector (spectrometer). The positions of the lines permit qualitative analysis of the sample. The relationship between line intensity and concentration permits quantitative analysis.

Spectral apparatus for AES consist of three main components: an excitation source, a monochromator and a detector.

Excitation sources have two main functions: conversion of the sample to the gas state, so that free atoms are present, and excitation of the sample so that it radiates light. The intensity of the spectral lines should be high and that of the background (see Plasma) should be low. Constant intensity of the lines is also desirable. The most important excitation sources used in A. are flames, electric arcs, high-voltage sparks and Inductively coupled plasma (see).

Flames are relatively low-energy sources, so they are used mainly for those elements which are readily excited. This technique is often considered a separate method, Flame spectrophotometry (see).

When excitation of an element to the point of light emission requires higher energy, *electric arcs* are used. The arc is created between two electrodes, one or both containing the sample. Either constant or alternating current, at 3 to 20 A, can be used to generate the arc plasma. Temperatures between 4000 and 7000 K are produced in the plasma. Because of the large amount of energy transfered, the electrodes become very hot. This permits vaporization and thus analysis of relatively non-volatile samples. However, for volatile substances (e.g. mercury or zinc), this is a disadvantage. For such materials, periods of cooling must be allowed. This is achieved by the use of intermittent arcs, which are periodically interrupted and spontaneously re-established. Because it consumes a large amount of material, the electric arc permits resolution of low concentrations, and is very suitable for trace analysis. For analysis of main components of samples, however, it is less suitable, because the measurements are not highly reproducible. The spectra generally contain only atom lines (fewer lines from ions). The arc spectra therefore contain relatively few lines and are good for qualitative analysis because there is little overlap.

A *high-voltage spark* is obtained by use of a transformer to produce about 10 kV direct current. This is used to charge variable-capacity capacitors. The high-voltage spark is produced by a brief discharge of the capacitor across a spark gap. The time course of this discharge is influenced by the capacity, self-induction and resistance of the oscillating circuit and the condition of the spark gap. In analysis, a series of individual sparks with identical time courses are discharged about every 10^{-2} s; each spark lasts about 10^{-4} to 10^{-5} s. The current density and thus the temperature in the spark plasma are very high ($\approx$ 100 A, $\approx 5 \cdot 10^4$ K). However, the average current density is much lower. The electrodes remain at a low temperature during the spark discharge. Because of the high temperature in the spark plasma, many ionic lines are seen in addition to the atomic lines, which makes the spectra less useful for qualitative analysis. Only a small amount of material is consumed in the high-voltage sparks, so that this method is not suitable for trace analysis. In addition, the low temperature of the electrodes makes excitation of non-volatile substances difficult. However, the reproducibility of a spark excitation is significantly better than that of an arc excitation, so the spark excitation is used mainly for quantitative analysis; both major and minor components can be studied.

Recently, *lasers* have also been applied for vaporization and excitation of samples; since the laser can be focused on a very small area of the surface, local analyses are possible.

The light coming from an excitation source is fo-

cused by a system of lenses on the entrance slit of a monochromator, where it is spectrally resolved by means of a prism or diffraction grating. The resolution required of the monochromator depends on the type of analysis being done. Much lower resolution is required for the relatively line-poor spectra of the alkali metals than for the spark spectra of samples containing numerous heavy metals, for example. For the latter purpose, high-resolution plane gratings are used.

The choice of optical material depends on the spectral region being measured. For the visible range, glass optics are suitable, but for the near UV (400 to 200 nm), quartz optics are needed. For studies in the far UV (below 200 nm), which are done mainly to determine elements such as sulfur, phosphorus or carbon, a vacuum grating apparatus is used.

The *detector* is either a photographic plate or a suitable photoelectric detector. The photographic plate has a number of advantages: it permits simultaneous measurement of wavelengths and intensities over the entire spectral range. For example, a single photograph is sufficient for analysis of an unknown sample containing many components. In addition, it is a permanent document of the analysis. The main disadvantage is that the analysis of the plates is cumbersome. Photoelectric detectors are increasingly being used for precise and rapid measurements. With secondary electron multipliers or photodiodes, for example, the process can be automated. Photoelectric detectors have the great advantage over photographic plates that there is a linear relation between the concentration and the voltage generated in the detector over a much broader range ($1:10^5$). In the simplest case, the photoelectric detector is applied to the exit slit of the monochromator. As the dispersive element is rotated (see Spectral apparatus), the various wavelengths pass through the slit and are registered by the detector (sequential analysis). Simultaneous determination of several elements requires a multichannel system which contains several photoelectric detectors, each placed to receive light of a certain wavelength. Devices with more than 30 secondary electron multipliers have been described for use in simultaneous multielemental analysis.

Sample preparation. A. is used mainly with solid and liquid samples. If a solid sample is an electrical conductor, it can be used directly as an electrode. The counter electrode can be made of the same material or of Fe, Cu or C. If the sample is nonconducting, graphite electrodes are used. A hole is bored in one electrode and filled with finely powdered sample. Nonconducting or inhomogeneous samples can be dissolved, which may be followed by concentration of trace elements or separation of interfering impurities. Solutions have the advantage over solids that the matrix effect is reduced, and the preparation of calibration samples is easier. There are various methods of applying the solution to the electrodes.

Applications of A.: Qualitative analysis. Since each type of atom emits a characteristic spectrum, the emission spectrum of a mixture (e.g. of an alloy) contains the characteristic spectra of all the individual components superimposed on each other. A. is therefore very well suited for multielement analysis. More than 70 elements can be determined with samples of only a few mg. An element can be detected simply by locating its characteristic lines in the complex spectrum; the lines used are the most intense, so that they are the last to disappear as the concentration decreases. The lack of a line is a rather reliable negative indicator. However, since the spectra can contain a large number of lines, the lines of different elements may coincide. Therefore a positive identification of an element requires the presence of several of its detection lines. The limits of detection of the method are summarized in the table.

Limits of detection of some elements with the direct current arc

Element	Analysis wavelength in nm	Limits of detection	
		percent	micrograms
Ag	328.1	0.0001	0.01
Ca	393.4	0.0001	0.01
Cd	228.8	0.001	0.1
Cu	324.7	0.00008	0.008
K	344.7	0.3	30
Mg	285.2	0.00004	0.0004
Na	589.6	0.0001	0.01
Zn	334.5	0.003	0.3

Quantitative analysis. The relation between light intensity and concentration is complicated, because the plasma contains atoms in both the ground and excited states and ions in an equilibrium which depends on the temperature. The fraction of ions is given by the Saha equation:

$$\frac{M_o}{N_o} = \frac{A}{N_e}(kT)^{5/2} e^{-E_i/kT}$$

Here M_0 is the concentration of the ions, N_0 the concentration of the atoms and N_e is the concentration of the electrons. E_i is the ionization energy, k the Boltzmann constant, T the absolute temperature and A is a constant. From this equation it can be seen that as the temperature increases, so do the numbers of ions, M_0, and electrons, N_e. At plasma temperatures up to 4000 K, the ion concentration can be ignored, however, and a simple Boltzmann distribution can be taken as the distribution of the atoms between the ground and excited states.

$$\frac{N_a}{N_g} = \frac{g_a}{g_g} e^{-E_a/kT}$$

Here N_a is the concentration of the atoms in the excited state, N_g is their concentration in the ground state, g_a and g_g are the statistical weights of the states, and E_a is the excitation energy. From equation (2), it can be seen that the concentration of atoms in excited states increases with increasing temperature. However, calculation shows that the fraction in excited states is small, even at high temperatures. For example, the ratio N_a/N_g for the resonance line of cesium at 2000 K is $4.44 \cdot 10^{-4}$; at 3000 K, $7.24 \cdot 10^{-3}$; at 4000 K, $2.98 \cdot 10^{-2}$, and at 5000 K, $6.82 \cdot 10^{-2}$. Thus even at 5000 K, there is only one atom in the excited state for every 682 in the ground state. Since the ratio N_a/N_g increases as the temperature rises, the intensity of the emitted light ought also to increase with temperature.

However, this is only partially correct, because the number of ions also increases, at the expense of the neutral atoms, and this leads to a loss of intensity of the atomic line. The increase in intensity to be expected from equation (2) occurs only so long as the concentration of ions is small. At high temperatures, the decrease in the number of neutral atoms outweighs the increase in intensity. Thus the line intensity passes through a temperature-dependent maximum, and the temperature of the maximum is different for each line of an element. This fact is very useful for identification of elements. The intensity I of the light emitted by the excited atoms is

$$I = h \cdot \nu \cdot N_a \cdot A \cdot V. \quad (3)$$

Here $h \cdot \nu$ is the energy of the photon, A the Einstein transition probability of the transition $N_a \rightarrow N_g$, and V is the volume. Substitution in equation (2) gives

$$I = h \cdot \nu = g_a/g_g \cdot N_g \cdot e^{-E_a/kT} \cdot A \cdot V \quad (4)$$

From this it can be seen that the intensity depends on the concentration of atoms in the plasma. Provided that the concentration of atoms in the plasma is proportional to their concentration C in the sample,

$$I = K \cdot C, \quad (5)$$

where K is a function of the temperature.

This equation is fulfilled only by very dilute plasmas. For real plasmas, there is no strict proportionality between the intensity and the concentration, because other factors affect the intensity. The most important of these are: 1) *self-absorption*, the reabsorption of primary emitted photons by atoms in the ground state; 2) *nonradiative transitions*, in which the excited atoms give up their energy of excitation by non-radiative processes, such as collisions; 3) *dissociation processes* which affect the formation of free atoms when the dissociation energies are high; and 4) *vaporization processes* of salts, which affect the number of atoms in the plasma. These processes are often affected by other elements in the sample (see Matrix effects).

Because of the factors discussed here, theoretical treatment of the relation between intensity and concentration is very difficult, and in general, quantitative analysis has an empirical basis. The empirical calibration function most commonly used today is

$$I = aC^b \quad (6)$$

where a reflects the effects of matrix and temperature, and b the effect of self absorption.

In most cases, however, the absolute intensities are not measured; instead, the signal is measured as the ratio of two intensities. The intensity of an analytical line is related to a reference line which can come from the sample itself or an additive, or to the spectral background.

$$I/I_R = a' \cdot c^{b'} \quad (7)$$

A typical *application* of quantitative A. is determination of many elements simultaneously in metal samples; for continuous quality control in production, the apparatus is automated. Compared to other methods of analysis, A. has an average lower limit of detection, average to good selectivity, a very wide range of application and the possibility of simultaneous multielement analysis. The disadvantages are the considerable expense, the time required when photographic plates are used, and the matrix-sensitive effects of temperature.

Atomic fluorescence spectrometry, ***AFS***: A technique using the fluorescence of free atoms for quantitative determination. The principle is shown in the block diagram of an atomic fluorescence spectrometer (Fig. 1).

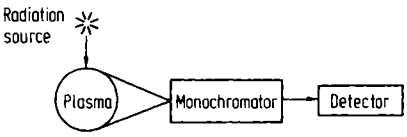


Fig. 1. Block diagram of an atomic fluorescence spectrometer.

An intense monochromatic beam of light from a dye laser or electrodeless discharge lamp is focused on a Plasma (see) which is generated by a low-background flame or electric heating. The sample is present in the plasma in the form of free atoms, most of which are in the ground state. The frequency ν of the excitation radiation is chosen so that its energy exactly corresponds to the excitation energy ΔE of the atom ($\Delta E = h\nu$; h is Planck's constant). Upon absorbing this light, the atoms enter an excited state, where they remain for a very short time ($\approx 10^{-8}$ s) before re-emitting all or part of the excitation energy in the form of fluorescence light as they return to the ground state or a lower excited state. The emitted fluorescence light is measured by a detector [e.g. a Photomultiplier (see)] at right angles to the exciting light, in order to avoid recording the latter. Since the fluorescence light can contain light of various wavelengths as well as scattered light, the fluorescence line used for analysis must be isolated by a monochromator. To eliminate interference by the emission of the flame, the excitation radiation is modulated so that only the fluorescence light resulting from it is registered by the detector.

There are 4 different types of fluorescence: 1) *Resonance fluorescence*, which occurs when the fluorescence light has the same wavelength as the absorbed radiation, permits the most sensitive detection. 2) *Direct line fluorescence* occurs at longer wavelengths than the absorbed radiation, because the fluorescing atom enters a lower excited state instead of returning to the ground state (Fig. 2). 3) *Stepped fluorescence* occurs when an atom in a higher excited state drops to the first excited state and then decays to the ground state by emission of fluorescence (Fig. 3). 4) *Sensitized fluorescence* occurs when the atom enters the excited state as a result of colliding with an excited atom of another element. For example, a plasma containing both Hg and Tl atoms, when irradiated with the Hg line at 253.7 nm, emits the two Tl lines at 377.6 and 535.0 nm.

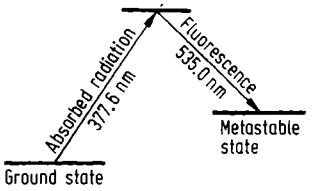


Fig. 2. Direct line fluorescence of thallium.

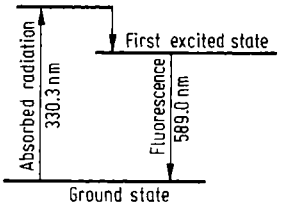


Fig. 3. Stepped fluorescence of the sodium ion.

The intensity of the fluorescence depends on the intensity of the exciting radiation, the fraction of the radiation absorbed by the atoms, the quantum yield of the fluorescence and the fraction of the fluorescent radiation which is reabsorbed by other atoms (self-quenching). For practical purposes, it is essential that the fluorescent radiation be proportional to the intensity of the exciting radiation and to the number of atoms in the absorbing plasma. If the quantum yield of the fluorescence is high, it can give an extremely sensitive method for detection of certain elements, which makes A. especially suitable for trace analyses.

The fluorescence measurements are evaluated using calibration curves, which are often linear with respect to the fluorescence intensity and concentration over a wide range. However, there are many factors which can cause errors and which have prevented wide use of A.

A. is used most often for detection of traces of such metals as Zn, Cd, Hg, Tl, Cu, Ag, Au, Pb and Mg, because at present the majority of instruments still use electrodeless discharge lamps for excitation. As dye lasers become more widely used, this selection will change.

Atomic heat: see Molar heat.

Atomic lattice: see Lattice type.

Atomic mass: 1) ***absolute A.***, the mass of an atom. It is too small (on the order of 10^{-24} to 10^{-22} g) to be measured directly, but it can be calculated for any element X as the quotient of its molar mass M_X divided by Avogadro's number N_A: $A_X = M_X/N_A$. Using this equation, the absolute A. of hydrogen, the mass of an H atom, is calculated as

$$A = \frac{1.008\,\mathrm{g\,mol^{-1}}}{6.023 \times 10^{23}\,\mathrm{mol^{-1}}} = 1.674 \times 10^{-24}\,\mathrm{g}$$

The absolute A. is an inconvenient parameter for calculations, and is rarely used in chemistry.

2) ***Relative A.***, A_r, is the ratio of the mass of an atom to 1/12 of the mass of the carbon isotope ^{12}C. The term *atomic weight* for A_r is based on a confusion of the terms mass and weight, and should not be used. The relative A. of an element X is the ratio of its absolute A. to a uniform reference mass, the *atomic mass unit u*:

$$\underline{A}_{r,x} = \frac{A_x}{u} \text{ with } u = \frac{1}{12}\,\underline{A}_{12C} = \frac{1}{12} \times 1.992 \times 10^{-23}\,\mathrm{g}$$

$= 1.660 \cdot 10^{-24}$ g. The relative A. of the elements are in the same ratios as their absolute A. Most chemical elements are mixtures of isotopes, in which the abundances of the individual isotopes are almost always in a constant ratio. The A. of such mixtures is therefore a weighted average: $A_{r,X} = \sum_i x_i A_{r,X_i}$, where x_i is the relative molar abundance (see Composition parameters) and A_{r,X_i} is the relative mass of each isotope of the element X. Relative A. were originally determined by measurements of gas densities and by very precise quantitative analyses of suitable compounds. In this way, the average relative masses of isotopically mixed elements were obtained. Higher precision is now possible by use of mass spectroscopy, which gives the relative A. of the individual isotopes.

Other relative masses such as the relative Molecular mass (see), Formula mass (see) and Equivalent mass (see) are defined analogously.

Historical. The term A. was introduced by J. Dalton around 1805 in connection with his atomic hypothesis and used in establishing the basic laws of stoichiometry. He assigned the value of 1 to the mass of the lightest element, hydrogen. In the further development of chemistry, oxygen compounds were most often used in the determination of relative A. It therefore seemed reasonable to express the value directly in terms of this element. In 1815, J.J. Berzelius used $A_{r,O} = 100$ for his table of atomic masses; however, this was not widely accepted. In order to retain the approximate value of 1 for the relative A. of hydrogen, the relative A. of oxygen was set equal to 16 on the suggestion of the Belgian chemist J.S. Stas. After the establishment of $A_{r,O} = 16.0000$ in 1905, the ratio of $A_{r,H}$:$A_{r,O}$ = 1.0080:16.0000. The choice of oxygen as the basis for the atomic mass scale proved problematic, however, when it was discovered that this element consists of small amounts of the heavier isotopes ^{17}O and ^{18}O in addition to the main isotope ^{16}O, and that the isotopic ratios can vary somewhat depending on the source of the oxygen. Therefore, in addition to the *chemical atomic mass scale* with the value $A_{r,O} = 16.0000$ for the natural isotope mixture, a *physical atomic mass scale* was introduced in which the mass of the isotope ^{16}O was the reference parameter. To convert the values for relative A. in the chemical scale to the physical scale, they had to be multiplied by the factor 1.000275. To remove this inconsistency, which caused considerable confusion, in 1961 a new international system was introduced: the carbon scale. In it, the isotope ^{12}C has an A_r of exactly 12. The values from the chemical oxygen scale had to be multiplied by 0.999957, and those from the physical scale by 0.999682, to convert them to the carbon scale.

The precise determination of relative A. by chemical methods owed much to the German chemist O. Honigschmid (1878-1945). The relative A. are still

subject to constant improvement in precision, and their latest values are published at intervals by a special commission of the IUPAC.

Atomic mass unit: see Atomic mass.

Atomic moment: see Dipole moment.

Atomic number, abb. ***Z***: originally, the number indicating the position of an element in the periodic system. The A. is equal to the number of protons in the nucleus, and, therefore, to the number of electrons in the neutral atom of an element. For this reason, it is also called the ***nuclear charge number***. The A. of the elements can be determined experimentally from the K_α x-ray lines (Moseley's law).

Atomic orbital: see Atom, models of.

Atomic polarization: see Polarization.

Atomic radius: a relative measure of the size of an atom. Since an atom is not a sharply limited system (see Atom, models of: quantum mechanical model), it is also not possible to give its size precisely. The following A. are defined: the ***covalent A.*** is equal to half the distance between identical atoms in an atomic bond. Covalent radii for the atoms depend on the bond order of the bond. The bond lengths of single or multiple bonds can thus be given approximately as the sums of the corresponding covalent A. The ***theoretical A.*** is the maximum of the radial distribution (see Atom, models of) of the outermost occupied orbital. The ***metallic A.*** is defined as half the distance between adjacent atoms in the crystal. This is usually referred to lattice types with coordination numbers of 12 (metal crystals). To estimate the spatial extent of a molecule, Stuart and Briegleb introduced the ***van der Waals A.***, which is also called the ***effective radius***. It approximates the action range of an atom in terms of Van der Waals bonding forces (see) of a molecule, and therefore permits estimates of intermolecular distances in molecular crystals. Van der Waals A. are larger than covalent A., and when used in models they show interpenetrating atomic spheres. These are the basis of the space-filling models which are very useful for visualizing molecular configurations and conformations in organic chemistry. The different definitions of A. lead to different absolute values for the same type of atom. However, the changes in the different types of A. throughout the periodic system generally show the same tendencies (Table). The A. are greatly changed by formation of ions. Cation radii are smaller, and anion radii are larger than those of the corresponding neutral atoms (see Ionic radius).

Atomic radii of some representative elements on pm

	Covalent atomic radius	Theoretical atomic radius	Metallic atomic radius	van der Waals atomic radius
H	30	53	.	120
Li	135	159	150 ... 155	.
Na	155	171	185 ... 190	.
K	195	216	235 ... 255	.
Mg	140	128	155 ... 160	.
Ca	.	169	190 ... 195	.
Sr	.	184	210 ... 215	.
Ba	.	206	220 ... 225	.
B	80 ... 90	78	.	.
Al	125 ... 130	131	140 ... 145	.
C	75 ... 85 (67, 60)*	60	.	125 ... 135
Si	117 (107, 100)*	107	135	170 ... 200
Sn	140	124	160	.
Pb	145	122	160 ... 175	.
N	70 ... 80 (60, 55)*	49	.	150
P	110 (100, 93)*	92	.	190
As	115 ... 120 (111)*	100	135 ... 150	200
Q	65 (55)*	41	.	130 ... 140
S	105 (94)*	81	.	155 ... 185
Se	115 (107)*	92	160	200
Te	130 ... 135 (127)*	121	170	220
F	65	36	.	135
Cl	100	73	.	180
Br	115	85	.	195
I	135	104	.	215

* Numbers in parentheses indicate covalent A. for double and triple bonds.

Atomization: the distribution of a liquid into fine droplets by spraying. It creates a large surface area, which accelerates interactions between the atomized liquid phase and the surrounding gas phase (acceleration of chemical reactions; for example, in the synthesis of ammonium sulfate, liquid sulfuric acid is atomized in an ammonia atmosphere; rapid heat exchange is achieved by spraying molten solids into areas where the temperature is below their melting point, and a fine-grained powder is obtained). In other cases, the desired result is the finest possible distribution of the liquid medium on a large surface (liquid fertilizers, hair spray and perfume atomizers). The A. of a liquid can also be used to bind and precipitate fine dust or ash. A. is also frequently used for drying (see Spray drying).

In a pressure atomizer, the liquid is pressed through an opening of 0.3 to 4 mm diameter by a pressure of 3 to 7 MPa. In a compressed air (or gas) atomizer, the liquid is carried through the valve by the stream of propellant gas. In centripetal or centrifugal atomizers, the liquid is sprayed off a disk which is rotating at a high speed - up to 250 m s^{-1}. Centripetal atomizers can be used to atomize even highly viscous solutions, suspensions and other liquids which would corrode or plug valves.

A. can also be achieved electrostatically. A high voltage is applied between the valve and a counterelectrode. This method is used for paint sprayers for painting metal objects; the object to be painted acts as the counter electrode.

Atomization drying: same as Spray drying (see).

Atomic spectroscopy: analysis of the electromagnetic spectra of free atoms. Since free atoms absorb and emit at the same wavelengths, atomic spectra can be observed as emission or absorption spectra, or as a combination of the two, as fluorescence spectra. An individual line is characterized by its frequency v, and corresponds to the energy difference ΔE between two defined energy states E_1 and E_2 of the atom in question:

$$\Delta E = E_2 - E_1 = h\nu \qquad (1)$$

In optical A., which is limited to the UV, visible and IR portions of the electromagnetic spectrum, these energy states correspond to different arrangements of the valence electrons. Electronic transitions of the inner electrons produce X-ray spectra (see X-ray spectroscopy). Only optical A. will be discussed here.

In order for a sample to exist as free atoms, it must be converted to a plasma before the spectrum is observed.

Theoretical. Since the spectra are specific for the type of atom which absorbs or emits them, they must be closely related to the structure and properties of the atoms. They are therefore interpreted in terms of a suitable model, either the Bohr-Sommerfeld or the quantum mechanical model. Comparison of spectra of different atomic spectra shows that the arrangement of the spectral lines is related to the position of the element in the periodic system. Elements with a single valence electron, e.g. the alkali metals, have relatively few lines in their spectra, whereas elements with several valence electrons, e.g. the transition elements, have numerous lines in their spectra. The simplest spectrum is that of the neutral hydrogen atom. It contains a succession of sharp lines which are closer together at shorter wavelengths (Fig. 1); such a group of lines is called a series. At the short-wavelength end, the lines converge on a position called the series limit.

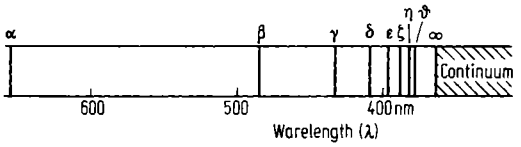


Fig. 1. Balmer series of the hydrogen spectrum.

On the other side of the series limit is a region of continuous absorption which arises from transitions of electrons from discrete energy states into energy states outside the atom, or conversely. The states outside the atom are not quantized, so the free electron can have any arbitrary amount of kinetic energy.

In the spectrum of atomic hydrogen, there are five series. The wavenumbers $\tilde{\nu}$ of all the lines of the hydrogen spectrum can be expressed by the equation

$$\tilde{\nu} = Z^2 R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

where m is the principal quantum number of the higher excited state, n is the principal quantum number of the lower excited state, R is the Rydberg constant (see) (109677.759 cm^{-1}) and Z is the nuclear charge number. The wavenumber of a spectral line is thus the difference between two expressions $T_n = R/n^2$ and $R_m = R/m^2$, which are called *terms*. They represent the energy states of the atom divided by hc (c is the velocity of light). A spectral series arises when a variable term R/m^2 is subtracted from a fixed term R/n^2; R/m varies as the quantum number m takes on a series of values. For hydrogen $Z = 1$; thus eq. 2 yields the following formulas:

Lyman series (in the UV)	$\tilde{\nu} = R \left(\frac{1}{1^2} - \frac{1}{m^2} \right)$	$m = 2, 3, 4 \ldots$ (3a)
Balmer series (in the visible)	$\tilde{\nu} = R \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$	$m = 3, 4, 5 \ldots$ (3b)
Paschen series (in the IR)	$\tilde{\nu} = R \left(\frac{1}{3^2} - \frac{1}{m^2} \right)$	$m = 4, 5, 6 \ldots$ (3c)
Bracket series (in the IR)	$\tilde{\nu} = R \left(\frac{1}{4^2} - \frac{1}{m^2} \right)$	$m = 5, 6, 7 \ldots$ (3d)
Pfund series (in the IR)	$\tilde{\nu} = R \left(\frac{1}{5^2} - \frac{1}{m^2} \right)$	$m = 6, 7, 8 \ldots$ (3e)

It is conventional to represent these relationships in graphic form, in a term scheme, where the individual terms are represented as horizontal lines, so that the distance between them is proportional to the wavenumber of the corresponding spectral line (Fig. 2). It can be seen how the terms get closer together as the series limit is approached.

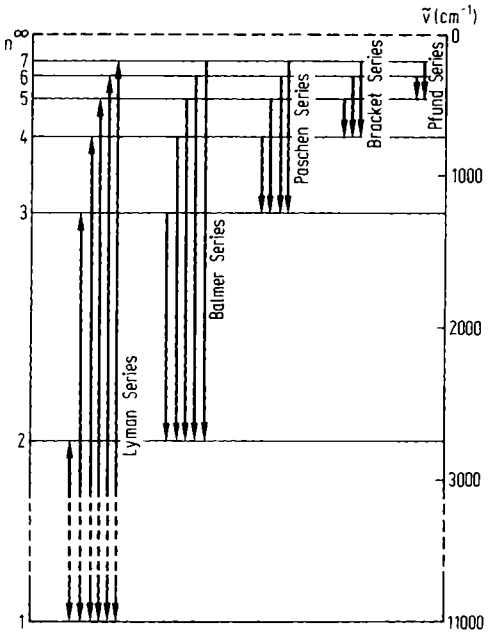


Fig. 2. Term scheme of the hydrogen atom showing spectral series.

The H atom should, in principle, be able both to emit and to absorb at all wavenumbers corresponding to transitions in Fig. 2. However, since H atoms are in the electronic ground state ($n = 1$) at normal temperatures, absorption is only possible for the Lyman series, in which the lower term is the ground state. The lines which end in the ground state are called resonance lines; they are the only ones which can be observed by both emission and absorption. All the other series are observed only as emissions, except when the atoms are already in an excited state.

The spectra of the helium ion He^+ and the lithium ion Li^{2+} are very similar to that of the hydrogen atom; each of these ions also has just one electron. In accordance with eq. 2, the spectral lines of the series of the He^+ ion ($Z = 2$) are at wavenumbers four times as large as those of the hydrogen spectrum, while the wavenumbers of the Li^{2+} lines ($Z = 3$) are nine times as large. These regularities are summarized in the

spectroscopic shift rule of Sommerfeld and Kossel, according to which the spectrum of any atom is similar to that of the singly charged positive ion of the following element in the periodic system, and of the doubly charged positive ion of the next element after that. Spectra of singly and multiply ionized atoms are called the first, second, etc. *spark spectra* because they are obtained from electric spark discharges. The spectrum of the neutral atom is called the *arc spectrum*, because it is usually observed in an electric arc. The spectra of alkali metals are relatively simple; the valence electron has a spectrum similar to the hydrogen spectrum. However, there are more energy states, and they cannot be described in terms of a single quantum number as the hydrogen states can. In addition to the principal quantum number, the following 3 quantum numbers are needed to describe these energy levels and the transitions between them:

- the secondary or orbital angular momentum quantum number l, which can have the values 0, 1, ..., n - 1; the corresponding electronic states are indicated by the letters s, p, d, f;
- the spin quantum number S, which can have the values +1/2 and - 1/2;
- the total angular momentum quantum number j, which is the vectorial sum of the orbital angular momentum and spin.

The various term series (Fig. 3) arise from different values of the orbital angular momentum (s, p, d, f). The observed series can be characterized as follows: principal series, s - np; sharp secondary series, p - ns; diffuse secondary series, p - nd; and fundamental (Bergmann) series, d - nf.

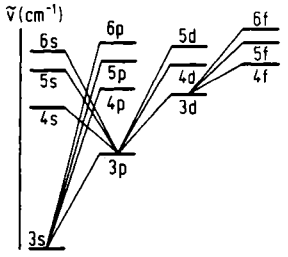


Fig. 3. Simplified term scheme for the sodium atom with the transitions corresponding to the various spectral series.

In the principal series the electron transitions occur between the p states of different principal quantum numbers n and the lowest s state (ground state); in the first secondary series they occur between the higher s states and the lowest p state, and so on. In contrast to the situation with the hydrogen atom, here the possible transitions between energy states do not all occur; there is a selection rule which requires that $\Delta l = \pm 1$. Closer inspection of the alkali metal spectra shows that all lines are actually double lines. This can be explained by the total angular momentum quantum number j. For $l = 1$, j can have the two values +1/2 and - 1/2 corresponding to the two possibilities for $s = \pm 1/2$. For $l = 0$, there is only a single possibility for s, so that $j = 1/2$. Therefore all terms except the s states are doublet terms, and the magnitude of the doublet splitting increases rapidly in the progression to alkali metals with higher atomic numbers. Only transitions in which $\Delta j = 0, \pm 1$ are allowed. This splitting of spectral lines into multiplets due to the quantized interaction between the orbital angular momentum and the spin is called fine structure.

In systems with several valence electrons, the complexity of the spectra increases further. The angular momenta l and s of the individual electrons add vectorially to give the total momenta L and S: l_1, l_2, l_3,...L and s_1, s_2, s_3... S. These then add vectorially according to the Russel-Saunders coupling to give the total angular momentum quantum number J.

There is a system of symbols denoting individual terms. For example, $3\,^2P_{3/2}$ indicates a state in which the principal quantum number is 3 and $L = 1$ (P). The left-hand superscript 2 indicates the multiplicity of the term $(2s+1)$, and the subscript 3/2, the value of J.

In the spectra of atoms with more than one valence electron, e.g. the alkaline earth metals, there are several term systems which in general do not combine with each other and which differ in their multiplicity. In the alkaline earth metals, which have 2 valence electrons, there are a singlet and a triplet system. Each system consists of a number of series similar to those of the alkaline earth metals. Another complication arises from the possibility of simultaneously exciting both valence electrons (double excitation). In general, even and odd multiplicities alternate through the periodic system (Table 1). Even numbers of electrons are associated with odd multiplicities, and vice versa (spectroscopic alternation). The facts mentioned above and others which have not been mentioned make the series character of most spectra, especially those of heavier elements, difficult to recognize, because the spectra are so complex.

Table 1. Spectroscopic alternation rule

Number of electrons	1	2	3	4	5	6	7
Multiplicity	2	1,3	2,4	1,3,5	2,4	1,3	2

At higher resolution, there is in addition to the fine structure a further, very slight splitting, called *hyperfine structure*. This is due to the interaction of electrons with the nucleus. It can occur because the element consists of several isotopes, or it can be due to an interaction with the nuclear spin (see NMR spectroscopy). The splitting of spectral lines in an external electric field is called the Stark effect (see), and the splitting in an external magnetic field is called the Zeeman effect (see).

Applications. A. can be used for qualitative and quantitative analysis. If an atom is elevated into an excited state, it can lose the energy of excitation by emission of a photon, which is the basis for Atomic emission spectroscopy (see) and Flame spectrophotometry (see). The absorption of photons is the basis of Atomic absorption spectroscopy (see). If the energy taken up by absorption of photons is reemitted in the form of a photon, the phenomenon is atomic fluorescence. The atomic spectroscopic analysis methods based on the processes of light emission and absorption are shown in Table 2.

Table 2. Atomic spectroscopic analysis methods

Sample	Plasma Main analytical generation	Excitation	Measured process	Methods
Solid or solution	Arc, spark Qualitative inductively coupled plasma	Electric (heat)	Emission	Emission spectroscopy AES
Solution	Flame Quantitative	Chemical (heat)	Emission	Flame spectrophotometry FSP
Solution	Flame Quantitative	Chemical, special light	Absorption	Atomic absorption spectroscopy

Atomic units: a system of measures based on atomic parameters. The unit of mass is the electron mass m_e, the unit of angular momentum is $\hbar = h/2\pi$ (h is Planck's constant), and the unit of charge is the charge of the electron e. Using the formula $e_\pi = e/\sqrt{4\pi\varepsilon_0}$ (ε_0 is the electric field constant), the energy is 1 Hartree = $e_\pi^4 m_e/\hbar^2 = 4.3593 \cdot 10^{-18}$ J. This is twice the ionization energy of the hydrogen atom. The A. of length is the radius of the first Bohr radius in the hydrogen atom (see Atom, models of): 1 $a_0 = \hbar/(m_e e_\pi)$ = 1 Bohr = 52.917 pm. Other parameters can also be given in terms of m_e, $\hbar$ and e. The use of A. is very convenient in quantum theoretical calculations for atoms and molecules, because the value of 1 is used for e, $\hbar$ and m_e in the equations. The use of A. also has the advantage that the results in this mass system are independent of corrections in the numerical values of the natural constants.

Atomic weight: see Atomic mass.

Atomization energy: see Bond energy.

Atom, models of: The current model of the structure of the atom has been constructed and revised over a period of time on the basis of experimental results. The earliest model, proposed by Dalton, was a rigid, homogeneous *sphere*. This model was used successfully to derive the basic equations of the kinetic theory of gases. The discoveries of the electron, proton and neutron indicated that the spherical model was incomplete. Rutherford's scattering experiments, in which α-particles (see Radioactivity) were deflected by thin gold foils, indicated that the atom has *structure*; this was corroborated by Lenard's electron-scattering experiments. The very existence of sub-atomic particles, as well as natural fission, indicate that the atom is not indivisible.

The ***Rutherford model*** was based on the results of α-particle scattering; it posits a very small *nucleus* with a radius of approximately 10^{-14}m. The nucleus contains Z positive unit charges and nearly the entire mass of the atom; it is surrounded by a cloud of Z *electrons* (in the neutral atom). The number Z corresponds to the atomic number of the element. The electrostatic attraction of unlike charges should cause the electrons and protons to adhere to each other. It was suggested that they could be separated because the electrons have kinetic energy and move around the nucleus in circular or elliptical orbits; the centrifugal force is compensated by the electrostatic attraction of the nucleus.

According to classical physics, the motion of an electron around the nucleus would give rise to an oscillating dipole, which would continuously emit energy. As it did, the orbit would steadily be reduced in size until the electron spiraled into the nucleus. It was clear not only that atoms do not emit light continuously (i.e. electrons do not spiral into the nucleus), but also that the emission of light from energetically excited atoms does not yield a continuous spectrum; instead, the light is emitted in discrete bands at certain wavelengths.

To resolve this dilemma, Bohr suggested that atomic electrons can move only in certain allowed orbits, or stationary states, and that they do not radiate energy so long as they remain in these states. In the ***Bohr model***, the allowed orbits are those in which the orbital angular momentum is an integral multiple of the natural constant $\hbar = h/2\pi$ (h = Planck's constant). In this way, Bohr arrived at the quantization of the orbital radii r_n and the energies E_n of electrons with quantum numbers n ($n = 1, 2, 3\ldots$). The smallest orbital radius ($n = 1$) for a hydrogen electron is the *Bohr atomic radius* $r_1 = a_0$ = 1 Bohr = 52.9 pm. This number is used as a unit of length in the system of atomic units. There is a definite energy associated with each orbit; and transition of an electron from one stationary state to another is associated with a change in its energy $\Delta E = E_n - E_m$, where m and n are the quantum numbers of the initial and final states. The energy is absorbed or emitted in the form of electromagnetic radiation with the frequency ν: $\Delta E = h\nu$. The electron energies calculated using the Bohr model can thus be used to predict the frequencies of light emitted or absorbed by atoms; for the hydrogen atom, the predicted frequencies agree very closely with those measured spectroscopically.

The Bohr model was refined by Sommerfeld, who included calculations for elliptical orbits; these require the introduction of another quantum number, and permit a theoretical explanation of the fine structure of the spectrum of the hydrogen atom. The great achievement of Bohr was the recognition that the electrons in an atom cannot have any arbitrary energy, but only discrete energy levels. Even though the Bohr postulates stand in contradiction to classical physics, and represent an arbitrary application of quantum conditions to the classical description of the electron, their heuristic value for the further development of atomic physics was immense. The difficulties of the Bohr model were first resolved by the development of a newer, more general quantum mechanical theory. This was the accomplishment of Schrödinger, Heisenberg, Born and de Broglie in the 1920s.

The ***quantum mechanical model*** is fundamentally a new conception of the atom. It is based on the dual nature of matter: photons, electrons and other submicroscopic particles have both particle and wave characteristics. This is expressed by the *de Broglie relation* $\lambda = h/p$, where the wavelength λ and momentum p of a particle are related by the Planck constant h. From this relationship follows a basic principle of the new theory: the *Heisenberg Uncertainty Principle*, which states that there is an unavoidable degree of uncertainty in the simultaneous determination of the location and momentum of a particle.

Mathematically, the uncertainty is expressed by the equation: $\Delta x \Delta p \geqq h$; the uncertainty in the location Δx and the momentum Δp must be at least as great as Planck's constant. For sub-microscopic objects like electrons and nucleons, therefore, an orbital curve cannot be determined. Thus the Bohr model violates the uncertainty principle by assigning definite orbits and velocities to the electrons. In the quantum mechanical model, orbits are replaced by *wave functions* which describe the behavior of the particle. For time-independent processes, the probability dW of finding a particle in the volume element $d\tau = dxdydz$ is given by the square of the wavefunction $|\Psi|^2 = \Psi^*(x,y,z) \cdot \Psi(x,y,z)d\tau$. $|\Psi|^2$ is the product of the wavefunction Ψ and its complex conjugate Ψ^*, and is called the *probability density*.

In addition to wavefunctions, *operators* $\hat{A}$, which are a form of mathematical prescription, are fundamental to quantum mechanics. It has been found that each physical parameter can be assigned an operator which, when applied to the wavefunction, yields the observable values in the form of *eigen values*. This is expressed by the equation $\hat{A}\Psi_n = A_n\Psi_n$. The functions Ψ_n are called the *eigen functions*, and the numbers A_n, the *eigen values* of the operator $\hat{A}$. The *eigen equation* for energy, called the *Schrödinger equation* after its inventor, is central to the quantum mechanical model of the atom. For a particle of mass m, it has the following form in cartesian coordinates:

$$\left[-\frac{h}{8\pi^2 m}\left(\frac{\delta^2}{\delta x^2}+\frac{\delta^2}{\delta y^2}+\frac{\delta^2}{\delta z^2}\right)+V_{(x,y,z)}\right]\Psi_{(x,y,z)} = E\Psi_{(x,y,z)}.$$

The expression in the square brackets is called the *Hamiltonian operator* $\hat{H}$. It represents the classical potential energy $V(x,y,z)$ of the particle and the second-order partial derivatives of the variables. The Schrödinger equation for the hydrogen atom can be solved exactly, if polar coordinates (r, ϑ, φ) are used instead of cartesian coordinates; in this way a very simple expression for the potential energy of the electron is obtained, and the variables can be separated. With the product expression $\Psi(r,\vartheta,\varphi) = R(r)\Theta(\vartheta)\phi(\varphi)$, the solution of the second-order partial differential equation with three variables is reduced to the solution of three corresponding differential equations with one variable each. It follows from the mathematical character of the Schrödinger equation and the physical boundary conditions that solutions exist only for certain wave functions Ψ_n (eigen functions) with the corresponding eigen values E_n for energy. The Ψ-functions, which describe stationary states of the electron, are called "*orbitals*". If they apply to electrons in an atom, they are called "*atomic orbitals*" (abb. *AO*). The wave functions, i.e. the atomic orbitals $\Psi_{n,l,ml}(r,\vartheta,\varphi)$ depend on the three variables r, ϑ, and φ, and in the hydrogen atom, or in the independent-particle approximation of the multi-electron atom (see Central field model, Electron configuration), they are determined by the three quantum numbers n, l, m. The quantum numbers can assume only certain values, which are related as follows: $n = 1, 2, 3...$; $l = 0, 1, 2..., n - 1$; $m_l = -l, -l+1, ... -1, 0, +1, ...l$. n is the *principal quantum number*, l is the *orbital momentum quantum number*, and m_l is the *magnetic quantum number*. l is the absolute value of the orbital angular momentum L_l and m_l is the component of L_l in the z direction.

Atomic orbitals with the same principal quantum number comprise a *shell*. For $n = 1,2,3...$, the letters K, L, M ... are used to designate the corresponding shells. Atomic orbitals with the same principal and orbital momentum quantum numbers comprise a *subshell*. The atomic orbitals with various l values are indicated by letters which are historical; for $l = 0,1,2,3$, the letters s, p, d and f are used (from the "sharp", "principal", "diffuse" and "fundamental" series of spectral lines of sodium). The symbols for atomic orbitals consist of a numeral indicating n and a letter indicating l, e.g. a state with $n = 3$ and $l = 1$ is a 3p atomic orbital.

In the hydrogen atom, the energy E_n of an electron depends only on the principal quantum number. Since for each value of n there are a total of n^2 states with the same energy, each energy level in the hydrogen atom is n^2-fold degenerate. Thus, for example, the 2s and 2p orbitals have the same energy. Graphic representation of the atomic orbitals $\Psi_{n,l,m}(r,\vartheta,\varphi)$ of the hydrogen atom, and especially of $|\Psi|^2$, which shows the electron densities around the nucleus, is very important for qualitative understanding of chemical bonding. However, for the sake of clarity, one is limited to partial representations. It is useful to write $\Psi_{n,l,m}(r,\vartheta,\varphi)$ as a product of a *radial function* $R_{n,l}(r)$ and an *angular function* $Y_{l,ml}(\vartheta,\varphi)$. The function $Y_{l,ml}(\vartheta,\varphi)$, normalized to 1, is called the spherical function. Real angular functions $Y_{real}(\vartheta,\varphi)$ are obtained by suitable linear combinations of the complex angular functions. The real functions have the advantage over the complex forms that their dependence on direction arises directly from the analytical expression. The $Y_{real}(\vartheta,\varphi)$ represent surfaces in space, and are usually represented as sections intersecting the xz or xy planes. They have different forms and orientations, depending on l and m_l (Fig. 1). The signs of the angular functions have no physical meaning, but they are useful for study of the symmetry properties of orbitals with regard to the electronic structure of molecules. The squares of the angular functions $Y_{real}^2(\varphi,\vartheta)$ are very similar in shape to the $Y_{real}(\varphi,\vartheta)$ and represent the distribution of the relative electron density over the surface of a sphere with a constant radius r. In general, there are l nodal surfaces ($Y_{real}^2 = 0$) in which the probability of electron occupation is 0. The parameter $4\pi r^2 R_{n,l}^2(r)$, called the *radial distribution*, is the most easily visualized. It gives the probability of finding the electron in a spherical shell

with the radius r and thickness dr. The maximum in the probability distribution of an electron in the 1s orbital of the hydrogen atom is found at the Bohr radius a_0 (Fig. 2). In contrast to the Bohr model, however, the quantum mechanical electron has a non-zero probability of being at another distance from the nucleus. As n increases, the maxima of the radial distribution functions are shifted towards larger values of r. There are also $n - l - 1$ radial nodal surfaces between $0 < r < \infty$. By themselves, the representations of the squares of the angular and radial partial functions give an incomplete picture of the distribution of the electron density in space. For a complete characterization of an electron in an atom, a fourth quantum number, the *spin quantum number* m_s (see Electron spin) is required. It represents the angular momentum of the electron's spin, and can have the values +1/2, - 1/2.

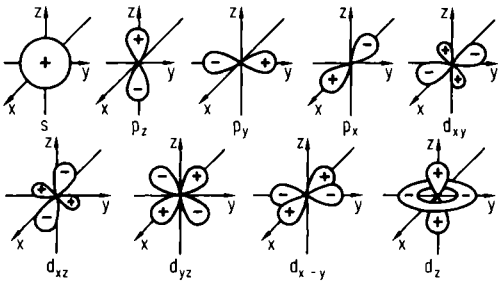


Fig. 1. Angular function Yreal (ϑ, φ). s, p, d ... indicate atomic states with the quantum number l = 0, 1, 2, ...

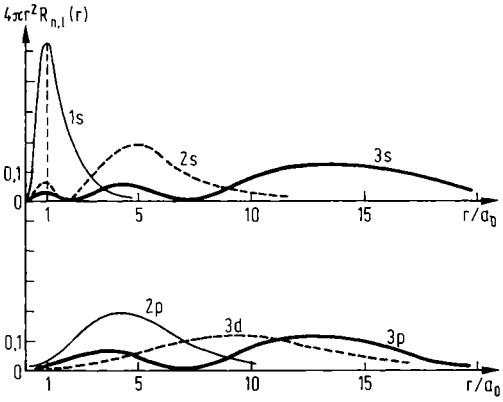


Fig. 2. Radial distribution of the electron in a hydrogen atom.

The insights into the electron structure of the hydrogen atom provided by the quantum mechanical model are used in the approximate treatment of multi-electron atoms (see Central field model). The advantage of the quantum mechanical model is its theoretical completeness, and the excellent agreement of its predictions with experimental results.

ATP: see Adenosine phosphates.

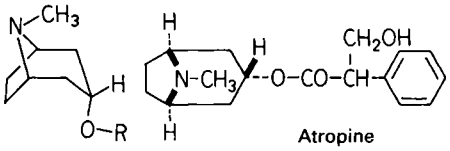
ATPases abb. for ***adenosine triphosphatases***: enzymes which catalyse hydrolysis of ATP to ADP and phosphoric acid. The energy released by the reaction (ΔH = - 30 kJ mol^{-1}) is used to drive most of the energy-requiring reactions in the cell.

Atramentization: see Phosphatization.

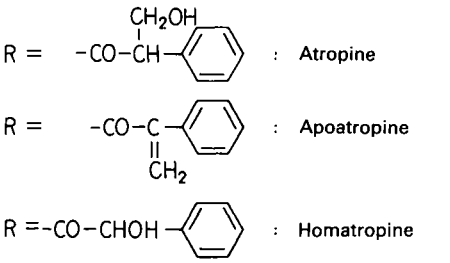
Atraton: see Triazine herbicides.

Atrazine: see Triazine herbicides.

Atropine: an ester alkaloid in which the OH group of Tropine (see) is esterified to the carboxyl group of R,S-tropaic acid. The tropaic acid component is a racemate of the naturally occurring S-hyoscyamine, in which the acid component has the S-configuration. ***S-Hyoscyamine*** forms crystalline needles; m.p. 109 °C, $[\alpha]_D^{20}$ - 22° (in 50% ethanol); ***atropine***, m.p. 118 °C, atropine sulfate, m.p. 194 °C. As ester alkaloids, A. and hyoscyamine are readily cleaved by hydrolysis. At higher temperatures, water is split off the tropaic acid component to form ***apoatropine***.



Atropine



A. is isolated from hyoscyamine-containing plants such as nightshade (*Atropa belladonna*), henbane (*Hyoscyamus niger*) and datura (*Datura stramonium*). The total alkaloid content of the leaves is 0.2 to 1% in nightshade, 0.04 to 0.08% in henbane, and 0.2 to 0.6% in datura. A. is a Parasympathicolytic (see). It is a neurotropic Spasmolytic (see), and the sulfate is used to relieve cramps in the abdominal and bronchial areas. It causes a long-lasting dilation of the pupils. In higher doses, it can cause undesired central effects. A. is the active ingredient of the belladonna extract. ***Homatropine*** is a partially synthetic derivative in which racemic mandelic acid is esterified to tropine. This has effects similar to those of A., but the pupil dilation does not last so long.

Historical. A. was independently isolated in 1833 by Main and by Geiger and Hesse. It was first synthesized by Wilstätter.

Atropine methobromide: a compound formed by quaternizing atropine with methyl bromide. A. is used as a spasmolytic. The central nervous effects of atropine are largely eliminated by the quaternization.

ATR technique: see Infrared spectroscopy.

Atropisomerism: a type of configurational isomerism which results when steric hindrance completely prevents rotation around a C-C single bond.

Enantiomers or diastereoisomers resulting from hindered rotation can be isolated if the rotation barrier at room temperature is above 85 kJ mol^{-1}. A. is observed in suitably substituted biphenyls (e.g. 6,6'-dinitrodiphenic acid), ansa compounds and cyclophanes.

Attractants: see Pheromones.

Attrinite: see Macerals.

Au: symbol for gold.

Auger electron spectroscopy, abb. ***AES***: a spectroscopic method for measuring the kinetic energy of secondary electrons (*Auger electrons*) emitted from a sample as a result of photoionization or electron collision ionization.

When atoms interact with X-rays or electron beams, electrons from inner shells are knocked out, leaving ionized atoms in excited states (see Photoelectron spectroscopy, X-ray spectroscopy). The resulting hole, e.g. in the K shell, is filled by an electron from a higher shell, such as the L_{II} shell. The energy released by this process,

$$E_K - E_{L_{II}},$$

can be emitted in the form of X-rays (X-ray fluorescence) or it may serve to release another electron (e.g. from the L_{III} shell), which takes with it the rest of the energy as kinetic energy. This produces an ion with a double positive charge. The kinetic energy of the Auger electron is approximately

$$E_{kin} \approx E_K - E_{L_{II}} - E_{L_{III}}.$$

Whether X-ray fluorescence or the Auger effect is more prominent in the deactivation of an excited state depends on the atomic number of the element. The Auger effect dominates in lighter elements.

Three electron states are involved in the process of Auger electron emission. The Auger electron is identified by adding the symbols of the electron states to that of the element. For example, in Mg-K $L_{II}L_{III}$, the first letter, K, indicates the level of the primary ionization of the magnesium atom, and the next two letters, L_{II} and L_{III}, the starting states of the electron which jumps into the inner shell and that of the Auger electron, respectively. The energy of the Auger electron corresponds to certain electron transitions, which are characteristic for the atom in question and are independent of the energy of excitation. It can therefore be used to identify a type of atom (qualitative analysis). Since the electron states are shifted slightly, depending on the bonding and the chemical environment of the atom, there is a chemical shift of the signal, just as in photoelectron spectroscopy. This is important for a detailed characterization of the position of the element in the sample molecules. Quantitative analyses may be made on the basis of the number of Auger electrons. Since Auger electrons can escape only from the uppermost layers of a solid sample, they can be used for analysis of very thin surface layers. This method is therefore especially well suited for surface studies, particularly for the study of such processes as catalysis, oxidation and corrosion.

August's formula: see Clausius-Clapeyron equation.

Auramine: $[(CH_3)_2N\text{-}C_6H_4]_2C{=}NH \cdot HCl \cdot H_2O$, a basic diphenylmethane dye. It is a bright yellow powder which is soluble in water and methanol; m.p. 136 °C. A. is used to dye paper, jute and coconut fibers; in medicine it is used to stain certain bacteria in sputum.

Aureolin: see Potassium hexanitritocobaltate(III).

Aureomycin®: see Tetracyclines.

Aurum: see Gold.

Austenite: a metallographic term for γ-iron, which is stable between 911 and 1392 °C, and for cubic face-centered γ-mixed crystals with a lattice constant of 356 pm of Iron-carbon alloys (see). A. with 0.8% carbon is stable above 723 °C, and at 1147 °C contains a maximum of 2.06% carbon. When cooled slowly, A. decomposes below 723 °C into Ferrite (see) and Cementite (see). Rapid cooling to room temperature leads in iron-carbon alloys to the formation of residual A. Addition of other alloy components, such as 18% chromium, 12% manganese and 8% nickel stabilizes the A. form in austenitic steels at low temperatures. A. was named for the English metallurgist Roberts-Austen.

Autocatalysis: a special case of Catalysis (see) in which a reaction product acts as a catalyst in the reaction. The reaction accelerates as it proceeds. Under certain conditions, A. can lead to bistability or to oscillations (see Oscillating reaction).

Autoclave: a vessel with pressure-resistant walls which can be closed air- and steam-tight and heated. The A. is equipped with a built-in thermometer and manometer, and sometimes also a stirring device. Substances can be heated to 400 °C and pressurized to 100 MPa in an A. The apparatus is used for reactions which do not give satisfactory yields under normal conditions. In medicine and biology, A. are used to sterilize equipment, growth media, drugs, etc. at 120 °C.

Autofining process: see Hydrorefining.

Autooxidation: oxidation of chemical compounds with atmospheric oxygen at room temperature or slightly above. In A., molecular oxygen is usually added to the oxidized molecules to form peroxide-like compounds; these then oxidize other molecules of the same or another substance. Substances which can be directly oxidized by molecular oxygen are called ***autooxidizers***; examples are sodium sulfite or hydrogen dissolved in palladium. If a substance can be oxidized only in the presence of an autooxidizer, it is called an acceptor, and it is oxidized by the peroxide-like intermediates of the autooxidizer. Some examples are ammonia, carbon monoxide, hydrogen iodide and oxalic acid. A. is initiated by a radical mechanism. Some industrially important A. are the oxidation of cumene (Hock's synthesis) and the drying of drying oils, such as linseed oil. Rusting of iron, ageing of rubber, resin formation in fuels and lubricants, rancidity in natural fats and oils and self-ignition of damp hay and straw are examples of undesired A. These processes can be inhibited or slowed by addition of antioxidants or stabilizers.

Autocide process: a method of exterminating insect pests by sterilizing them, e.g. by using Chemosterilizers (see).

Auwers-Skita rule: a rule for determining the configuration of *cis,trans*-isomers (see Stereoisomerism,

1.2.3) from physical properties (boiling point, index of refraction, density). The rule was established by Auwers and Skita between 1920 and 1923, and has been modified and limited since then. The modern form of the rule is that for alicyclic diastereomers with nearly identical dipole moments, the less stable isomer has the higher density, the higher index of refraction and the higher boiling point.

Auxins: a group of natural and synthetic growth regulators which stimulate cell division and cell extension in plants. The A. can either promote or inhibit growth, depending on the amount applied and the stage of development of the plant. The most important A. is Indol-3-ylacetic acid (see). Some important synthetic A. are indolyl-3-butyric acid, 1-naphthylacetic acid and 2,4-dichlorophenoxyacetic acid (2,4-D). Natural A. are formed mainly in rapidly growing tissues, especially at the tips of shoots and in young leaves and fruiting nodes. A. is used to promote the rooting of cuttings and setting of fruit, to thin fruits on trees, to inhibit growth of shoots in stored potatoes, and for defoliation. Some synthetic A. (2,4-D and 4-chlorophenoxyacetic acid) are also used as herbicides.

Auxochromes, ***auxochromic groups***: substituents with electron lone pairs which, when introduced into a colored compound (see Chromophores), increase the intensity and shift the wavelength of its absorption to longer wavelengths (see Bathochromicity). Some basic A. are $-NH_2$, $-N(CH_3)_2$, -NHR, $-NR_2$ (but not NH_3^+); some acidic A. are -OH, -OR and -OCOR. A pigment is not useful as a color-fast dye for fabric without such substituents; the basic or acidic properties of various A. give dyes the ability to bind to different fibers. However, the A. changes the color of the pigment by shifting its absorption. For example, quinone (yellow) → anilinoquinone (dark brown); dibenzoylethylene (colorless) → indigo (dark blue).

Avicides: poisons used to combat pest species of birds (e.g. crows or starlings). Some examples of A. set out in bait are strychnine (as poisoned wheat), yellow phosphorus (as poisoned eggs) and 3-halogen-*p*-toluidine. In some countries, thiophosphates of the same types as Organophosphate insecticides (see) are used either as bait or as area sprays.

A. are not so commonly used as Bird repellents (see). In addition to protecting newly sown crops and harvests from bird damage, they are used in cities, airports and rest areas used by migratory birds.

Avogadro's law: a basic law of stoichiometry: equal volumes of different gases at the same temperature and pressure contain the same number of particles (A. Avogadro, 1811). The particles postulated by Avogadro are molecules.

The discovery of A. was of great importance for the development of chemistry because, together with the Chemical volume law of Gay-Lussac (see), it made possible determination of the ratios of atoms in the molecules of gaseous compounds. It is a limiting law, and applies rigorously only to ideal gases.

Avogadro's number, N_A: the number of particles or elementary objects in 1 mol (see Mole). The best available numerical value is $(6.023045 \pm 0.000028) \cdot 10^{23}$. When used with the dimension mol^{-1}, A. becomes "Avogadro's constant".

A. is a proportionality factor linking molar with molecular parameters, $M = N_A \cdot m$, $V_M = N_A \cdot \varphi$, $R = N_A \cdot k$, $F = N_A \cdot e_0$, $E_\gamma = N_A \cdot h \cdot \nu$, etc. ($M$ is the molar mass, m the mass of a molecule, V_M the molar volume, φ the mean volume occupied by a molecule, R the general gas constant, k the Boltzmann constant, F the Faraday constant, e_0 the unit of electric charge, and E_ν the energy of 1 mol light quanta $h \cdot \nu$

Axerophthol: see Vitamin A.

Axial bond: see Stereoisomerism 2.2.

Aza[18]annulene pigments: a group of pigments in which the colored element is a cyclic system of conjugated double bonds with 18 π electrons. The most important examples are heme and chlorophyll; the synthetic phthalocyanin pigments are also A.

Azacyanine: see Cyanine pigments.

9-Azafluorene: same as Carbazole (see).

Azalene: see Pseudoazulenes.

Azamethonium bromide: see Ganglion blockers.

Azaserine: O-diazoacetyl-L-serine,

$$\underline{N}{=}\dot{N}\text{-}\underline{C}H\text{-}CO\text{-}O\text{-}CH_2\text{-}CH(NH_2)\text{-}COOH,$$

an antibiotic synthesized by *Streptomyces* species; it was formerly used as an antineoplastic drug.

Azathioprine: see 6-Mercaptopurine.

Azeotropic distillation: a process of distillation used to separate azeotropes or mixtures of liquids with very similar boiling points which cannot be separated by rectification. The equilibrium curve of liquid mixtures which do not obey Raoult's and Dalton's laws has either an azeotropic point P at which x (molar fraction of the more volatile component in the liquid) is equal to y (molar fraction of this component in the vapor), or the curve approaches the diagonal asymptotically at the upper or lower end. Separation of these mixtures beyond this point is only possible under certain conditions.

There are two methods of A. 1) A change of the pressure of the system (vacuum or overpressure) influences the phase equilibrium, so that the azeotropic point is shifted (Fig. 1). The separation of the mixture is carried out at a succession of different pressures. 2) Another form of separation is based on addition of another component. In this case, an azeotrope between the added component and the component to be

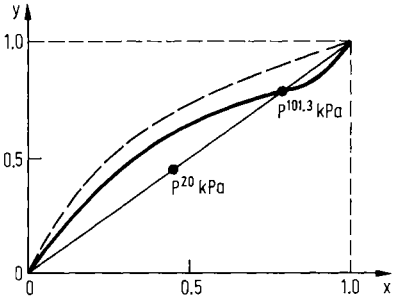


Fig. 1. Equilibrium diagram of an azeotropic mixture with the azeotropic point P. ____ Equilibrium line with the selective solvent; _____ Equilibrium line without the selective solvent.

removed is deliberately created. The boiling point of this azeotrope is sufficiently different from that of the original mixture that it readily distills over; the added component must also be chosen, however, so that it can readily be removed from the azeotropic condensate.

An example of A. is the drying of ethanol by addition of benzene. At first a ternary azeotrope of 18.5% ethanol, 74.1% benzene and 7.4% water boils off at 64.9 °C, then a binary ethanol/benzene azeotrope (b.p. 68.2 °C). The benzene or toluene is removed from the condensed fraction by A. with acetone or methanol (Fig. 2).

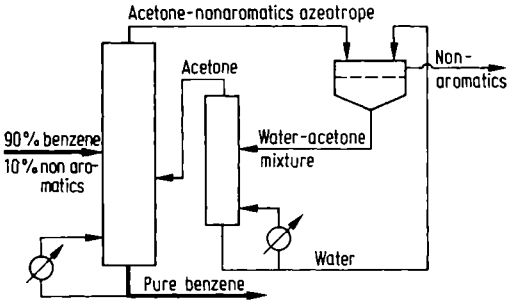
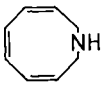


Fig. 2. Production of pure benzene by azeotropic distillation with acetone as selective solvent.

This A. is economical when small amounts (<10%) of nonaromatics are to be separated from the aromatic fraction, because in this case the major portion does not need to be vaporized. Extractive distillation is advantageous when the content of aromatics is between 90 and 60%. For aromatic contents < 60%, only liquid-liquid extraction is economical.

Azeotropic mixture: a mixture of two or more liquids which has a constant boiling point different from the boiling points of the individual components. A. cannot be separated by simple distillation. See Azeotropic distillation.

Azepines: seven-membered, heterocyclic compounds containing one nitrogen atom and three double bonds in the ring. They are antiaromatic and nonplanar, and therefore act as polyenes.



1H-Azepine

Azetidine, ***trimethylenimine***: a saturated, four-membered heterocyclic compound with a nitrogen atom in the ring; b.p. 63 °C, n_D^{25} 1.4287. The doubly unsaturated analogs are called ***azetes***, and the monounsaturated compounds are ***azetines***. A. can be synthesized by cleavage of hydrogen halides out of γ-halogen amines. Their properties are very similar to those of the aziridines. Azetidin-2-ones are also β-lactams and can be obtained by removal of water from β-aminocarboxylic acids. Another possible method of synthesis is cycloaddition of ketenes to azomethines. Azetidin-2-ones can be reduced to A.

Azidamphenicol: see Chloramphenicol.

Azides: derivatives of hydrazoic acid, HN_3.

1) Inorganic A. a) Salts with the general formula M^IN_3. *Ionic A.* are based on the azide ion,

$$\bar{\underline{N}}=\underline{N}=\bar{\underline{N}} \longleftrightarrow |\,N\equiv\overset{+}{\underline{N}}-\overset{2-}{\underline{N}}\,| \longleftrightarrow |\,\overset{2-}{\underline{N}}-\overset{+}{N}\equiv N\,|$$

which is a resonance-stabilized, linearly symmetrical structure. Because of its halide-like behavior, it is considered a Pseudohalide (see). The ionic A. formed with the most electropositive elements, e.g. Sodium azide (see), are relatively stable. However, because of a considerable covalent contribution and loss of symmetry of the anion, the heavy metal A. are highly explosive. The A. of lead and mercury explode on impact, and are therefore used as ignition explosives. The heavy metal A. are made by reaction of the corresponding metal salt solutions with sodium A. b) In nonmetal A., one or more A. groups are bound *covalently* to the nonmetal atom. Some well known examples are the unstable hydrazoic acid, HN_3, the A. of boron (Boron triazide, $B(N_3)_3$) and silicon (silicon tetraazide, $Si(N_3)_4$) and halogen A. of the type XN_3.

2) Organic A. a) Compounds with the general formula R-N=N=N. The names of these compounds are constructed from the names of the alkyl, aryl or heterocyclic groups R and the functional term "azide", as in phenyl azide, C_6H_5-N_3, or, if the molecule contains a higher-priority functional group, the name is constructed from the prefix "azido-" and the name of the root compound, e.g. azidobenzenesulfonic acid.

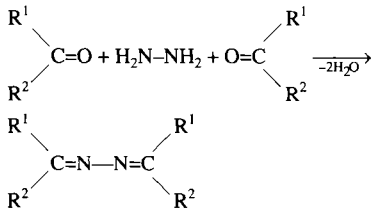
Low-molecular-weight A. are very unstable, and highly explosive. They are often processed only in the form of their dilute solutions. ***Aliphatic A. (alkyl A.)*** can be synthesized by reaction of haloalkanes with alkali azides, or from diazoalkanes and hydrazoic acid:

$$R\text{–}\bar{C}H\text{–}\overset{+}{N}\equiv N + H_3N \longrightarrow R\text{–}CH_2\text{–}N_3 + N_2$$

Aromatic A. (aryl A.) are made by reaction of arene diazonium salts with alkali azides or by the reaction of nitrous acid with aryl hydrazines: Ar-NH-NH_2 + O=N-OH → Ar-N_3 + 2 H_2O. Aryl azides react with hydrogen chloride to form N-chloroamines, which are easily rearranged to form chloroanilines. Some other important reactions of the A. are 1,3-dipolar cycloaddition to unsaturated compounds, forming triazoles, and photolytic or thermolytic cleavage into nitrenes and nitrogen. b) Compounds with the general formula R-CO-N_3 are called ***Acyl A.*** (see).

Azine: 1) an incorrect group name for derivatives of phenazine; see Azine pigments.

2) The systematic name for biscondensation products of hydrazine with carbonyl compounds. Aldehydes form ***aldazines***, while ketones form ***ketazines***.



3) A collective term for six-membered, heterocyclic compounds with at least one nitrogen atom in the ring. If several nitrogen atoms are present in the same ring system, the compounds are called Diazines (see), Triazines (see) or Tetrazines (see). If the ring system contains oxygen in addition to nitrogen, the compound is an Oxazine (see), and if both N and S are present, it is a Thiazine (see).

Azine pigments, ***phenazine pigments***: a large group of synthetic pigments which have a phenazine ring as the common chromophore. The A. can be either acidic or basic. 1) ***Quinoxalines*** are synthesized from 2-quinones and 2-diamines. 2) ***Eurhodines*** and ***eurodols*** are produced by co-oxidation of 4-diamines or aminophenols and 3-diamines or 3-dihydroxy compounds, or by condensation of 4-nitroso compounds of secondary and tertiary aromatic amines with 3-diamines. 3) ***Aposafranines*** are made by condensation of aminoazo pigments with aromatic amines. 4) ***Safranines*** are produced by co-oxidation of 4-diamines and monoamines. 5) ***Induline*** (see Induline pigments) and ***nigrosines*** are produced by heating aminoazobenzene with amines.

Azinphos-methyl: see Organophosphate insecticides (Table 3).

Aziridine, ***ethyleneimine***: a saturated, three-membered heterocycle with a nitrogen atom in the ring. A. is a colorless liquid, b.p. 56 °C, with an odor like that of ammonia. It is easily ignited and fumes in the air. It is poisonous, very caustic and carcinogenic. Because of the high ring tension, it is very reactive and can polymerize explosively to polyethylenimine. A. can be alkylated and acylated. It is synthesized by treating ethanolamine hydrochloride with thionyl chloride, which yields β-chloroethylamine hydrochloride. When this compound is heated with sodium hydroxide, A. is produced. A. can be used to introduce the aminoethyl group into organic compounds. It is used in the synthesis of drugs and to modify synthetic polymers.

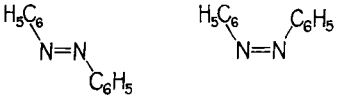
Azirine: an unsaturated, three-membered heterocyclic compound with a nitrogen atom in the ring. If the double bond is between the two carbon atoms, the compound is called 1H-A.; otherwise, it is 2H-A.

1H-Azirine

Azlactones: see Oxazolinones.

Azlocillin: see Penicillins.

Azobenzene: the simplest aromatic azo compound. A. exists in two stereoisomeric forms; the E-form is stable.



E- or trans-form Z- or cis-form

It crystallizes in red leaflets; m.p. 68 °C. When a solution of (E)-A. is irradiated with UV light, an equilibrium between the E- and Z-forms is established. (Z)-A. can be separated from the mixture of isomers by chromatography; m.p. 71.4 °C, b.p. 297 °C [E- and Z-form]. A. is nearly insoluble in water, but dissolves readily in hot alcohol and ether. It is poisonous, and in larger amounts has the same effects as nitrobenzene. In the presence of reducing agents, A. is converted to hydrazobenzene or aniline. It is oxidized with peracetic acid to azoxybenzene. It is obtained by reduction of nitrobenzene, oxidation of hydrazobenzene or condensation of nitrosobenzene with aniline. A. is used in the synthesis of dyes.

α,α'-Azobisisobutyronitrile, ***2,2'-azobis(2-methylpropionitrile)***: $(CH_3)_2C(CN)\text{-}N{=}N\text{-}C(CN)(CH_3)_2$, a poisonous, colorless, crystalline compound, m.p. 105 °C (dec.). α-,α'-A. is insoluble in water but soluble in most organic solvents; when an acetone solution of α,α'-A. is heated, it can explode. Above 35 °C, the compound decomposes, splitting out nitrogen and forming radicals. It is therefore used to initiate radical reactions. α,α'-A. is made by oxidation of the hydrazo compound.

Azo compounds: organic compounds containing the azo group, -N=N-, bound to the C atom of an aliphatic, aromatic or heterocyclic skeleton. A. can be oxidized to Azoxy compounds (see). The simplest representatives of the aliphatic and aromatic A. are Azomethane (see) and Azobenzene (see), respectively. The Azo pigments (see) are industrially important.

Azo coupling: the linking of arene diazonium salts with aromatic amines or phenols to form diazoamino or azo compounds.

Arene diazonium salts are electrophilic reagents which react with primary and secondary aromatic amines in weakly acidic solution to form diazoamino compounds or 1,3-diaryl triazenes:

$$R\text{–}\overset{+}{N}{\equiv}N| + H_2N\text{–}R \xrightarrow[-H^+]{} R\text{–}N{\equiv}N\text{–}NH\text{–}R.$$

These can undergo diazoamino-aminoazo rearrangement (see 4-Aminoazobenzene) to form aminoazo compounds.

With tertiary aromatic amines, diazonium salts couple directly to yield azo compounds:

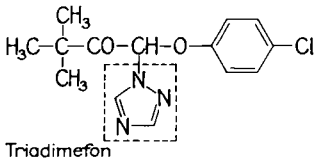
$$R\text{–}\overset{+}{N}{\equiv}N| + C_6H_5\text{–}O^- \rightarrow R\text{–}N{=}N\text{–}C_6H_5\text{–}OH$$

Arene diazonium salts can also react with CH-acidic compounds such as β-ketoesters and β-diketones in an A. The azo compounds formed in such reactions rearrange to form hydrazones. A. is a very common reaction, especially in the chemistry of the azo pigments.

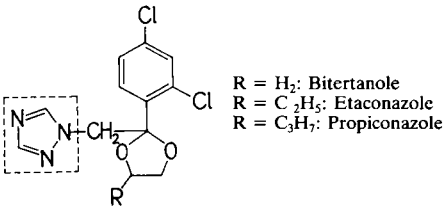
Azodicarboxylic acid esters: aliphatic azo compounds with the general formula ROOC-N=N-COOR. Most A. are yellow, unstable compounds which can decompose when distilled with a violent detonation. They are synthesized from chloroformate esters and hydrazine. The product of the first reaction step is a hydrazine *N,N'*-dicarboxylate which is converted to A. by oxidation with nitric acid or chlorine. A. are important in organic syntheses.

Azole: a five-membered heterocyclic compound containing 1 to 5 nitrogen atoms in the ring: Pyrazole (see) has two N atoms, Triazole (see) has three, and Tetrazole (see) has four. The ring may also contain other heteroatoms such as oxygen, sulfur or selenium.

Azole fungicides: Systemic Fungicides (see) based on imidazole or triazole. The most important imidazole type fungicide is *imazalil* [1-(β-allyloxy-2,4-dichlorophenylethyl)-imidazole], which is used against rose mildew and as a component in seed treatment for grains. The most important of the triazole types is *triadimefon*, m.p. 82.3 °C, p.o. $LD_{50} \approx 460$ mg/kg rat. This is used against mildews and rusts; it is synthesized from pinacolone. If the carbonyl group of triadimefon is reduced to the alcohol, the product is *triadimenole* (m.p. 112 °C, p.o. $LD_{50} \approx 950$ mg/kg rat). If the 4-terminal chlorine atom in this compound is replaced by a phenyl group, the systemic effect is weaker, but the action spectrum is broadened, and the protective and curative properties are still good: *bitertanole* (m.p. 123 to 129 °C; p.o. $LD_{50} > 5000$ mg/kg rat). *Propiconazole* and *etaconazole* are further modifications.



Triadimefon



R = H_2: Bitertanole
R = C_2H_5: Etaconazole
R = C_3H_7: Propiconazole

Azolides: see Azomethines.

Azoimide: same as Hydrazoic acid (see).

Azomethane, ***dimethyldiimide***: CH_3-N=N-CH_3, a colorless to slightly yellow gas; m.p. - 78 °C, b.p. 1.5 °C. A. is soluble in alcohol, ether and acetone. It can be made by oxidation of *N,N'*-dimethylhydrazine with copper(II) chloride.

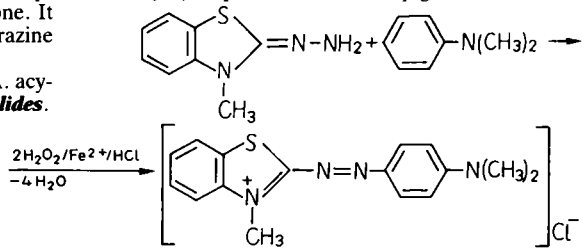
Azomethines: same as Schiff's bases (see). A. acylated on the ring nitrogen atoms are called ***azolides***.

Azo pigments: a large class of synthetic pigments which contain azo groups bound to sp^2-hybridized carbon atoms. The azo groups are usually bound to benzene or naphthene rings, but in some A. they are bound to heterocycles or enolizable aliphatic compounds. The number of azo groups is indicated by the prefix mono-, di-, tri-, etc. The color depends on the structure of the A. Monoazo pigments, e.g. 4-aminoazobenzene (Fig.), absorb only in the short-wavelength range because their delocalized electron systems are small; therefore, they appear yellow or orange. The introduction of more azo groups produces red, green, blue and black pigments. The color-deepening effect (see Bathochromic shift) can be intensified by introduction of condensed ring systems. The great variety of A. is also due to the introduction of substituents into the rings to which the azo groups are attached; -OH, -COOH, $-SO_3H$, $-NO_2$, alkyl or alkoxy groups, halogens, etc. are used. The number of A. produced in the laboratory is probably well over 100,000, although only a fraction of these are produced on a large scale.

Most A. are synthesized in two steps. First a primary aromatic amine is diazotized to make a diazonium salt, and this is then "coupled" with a suitable second component. These coupling reactions (see Azo coupling) are sometimes carried out in acidic media, and sometimes in alkaline media. The second component can be an aromatic amine or phenol, or their sulfonic or carboxylic acid derivatives (e.g. the alphabet acids). A. can also be synthesized by oxidative coupling of hydrazones with activated aromatic compounds.

4-Aminoazobenzene

The A. are used as acid, mordant and direct dyes for wool, cotton, rayon, silk and synthetic fibers. Some are also used as food colorings. Diazo pigments usually have darker colors than the monoazo pigments, and are the most numerous group of A. Because of their greater molar masses, they are much better direct dyes than the monoazo pigments. The first and best known, although not the most significant, diazo pigment is congo red. Most triazo pigments are already rather complicated structurally; and are too insoluble in water to be used in traditional dyeing processes. Instead, the fibers are dyed with a diazo pigment which contains a free amino group; this is then diazotized and coupled to another component, such as pyrazolone or β-naphthol derivatives (development dyes) to produce the triazo pigment.

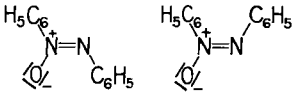


Synthesis of azo pigments by oxidative coupling.

Azote: French for nitrogen.

Azotometer: a gas buret for measurement of nitrogen volumes in elemental analysis. The A. consists of a calibrated measuring tube with a glass stopcock at the upper end. At the lower end of the tube there is a wide glass vessel with connections to a leveling vessel and the gas inlet. The A. is filled with very pure, 50% potassium hydroxide solution. The gas coming out of the combustion apparatus (CO_2 and N_2) is introduced into the A. CO_2 and H_2O are absorbed by the potassium hydroxide solution, while the nitrogen collects in the upper part of the tube. Its volume can be read, and after reduction to standard conditions, can be used to calculate the mass.

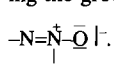
Azoxybenzene: the simplest aromatic azoxy compound. A. exists in two stereoisomeric forms, the Z or *cis*-form and the E or *trans*-form.



Z-form E- form

The more stable Z-form of A. crystallizes in light yellow needles; m.p. 36 °C. The (E) isomer forms colorless crystalline needles; m.p. 87 °C. A. is insoluble in water, but soluble in alcohol, ether and ligroin. It is formed by mild reduction of nitrobenzene in alkaline solution with glucose. Reduction of the stereoisomeric forms of A. with lithium alanate produces (E)-A. A. is important in the dye industry, and is also used for organic syntheses.

Azoxy compounds: aromatic compounds containing the group



A. are oxidation products of azo compounds. When heated in sulfuric acid, they undergo Wallach rearrangement (see), forming 4-hydroxyazo compounds. The simplest A. is Azoxybenzene (see).

Azulenes: bicyclic, non-benzoid, aromatic hydrocarbons. They are colored, usually blue. The structure consists of a fused cyclopentadiene and cycloheptatriene ring system in which two carbon atoms are shared by the two rings. This ring system contains ten C atoms and has 10 π-electrons in a planar arrangement, and thus has the typical properties of an aromatic compound. The parent compound, *azulene*, crystallizes in blue-violet leaflets, m.p. 99-100 °C, b.p. 115-135 °C at 1.33 kPa. Since 1955, its synthesis from Zincke aldehyde and cyclopenta-1,3-diene has been known. An intermediate of this reaction is fulvene, which is cyclized to A.

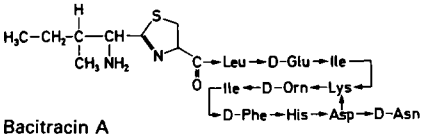
A. are termed non-alternating hydrocarbons, which means that the electron density distributions on individual C atoms are different. The electron density is particularly high at positions 1 and 3 (in the five-membered ring), so that electrophilic reactions occur there; examples are nitrations, sulfonations and Vilsmeier formylations. These different electron distributions are also reflected by the fact that A. has a dipole moment of about 1 D. Derivatives of the blue, crystalline parent compound are found in many essential oils, e.g. camomile oil, geranium oil and vetiver oil (see Guaiazulene and Vetiverazulene). A. have mild antiseptic effects, and are used in cosmetics such as toothpaste, soaps and skin cremes.

B

B: symbol for boron.

Ba: symbol for barium.

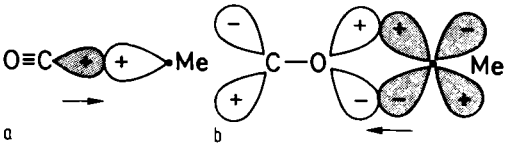
Bacitracins: peptide antibiotics produced by *Bacillus licheniformis*. The most important of them is ***bacitracin A*** (Fig.), a dodecapeptide with a thiazole structure as a heterocomponent. The thiazole is formed from the *N*-terminal isoleucine and the neighboring cysteine. The commercial preparation contains about 70% bacitracin A, and is used to treat superficial infections. B. are effective against gram-positive bacteria.



Bacitracin A

B. A forms a complex with undecaprenylpyrophosphate, a molecule which ferries hydrophilic cell-wall components across the bacterial plasmalemma, and prevents its enzymatic hydrolysis to the corresponding orthophosphate ester. This inhibits formation of the cell wall, and thus growth, of the bacteria. An intact thiazole ring and the histidine group are essential for the action of B.

Back bonding: a bonding model based on molecular orbital theory. In B., two parts of a molecule which are linked by a covalent bond display additional π-orbital interaction in which d orbitals are involved. It leads to charge equalization and thus to stabilization of the molecular system. The concept of B. is especially useful for explaining the bonding and stability of complex compounds of the transition metals, e.g. the metal carbonyls (Fig.).



Bond model for metal carbonyls:
a, donor bond; *b*, back bonding

Overlap of an occupied σ-orbital of the CO molecule and an empty d-orbital of the metal atom produces a charge transfer from the ligand to the central atom (electron donor σ-bond, Fig. a). In addition, the π^*-orbital (see Molecular orbital theory) of the CO molecule is a low-energy, unoccupied π-molecular orbital and can form an electron-acceptor π-bond (Fig. b) with an occupied π-type d orbital on the central atom (Fig. b). Thus there is a simultaneous transfer of an electron from the central atom to the ligand. This charge transfer from the central atom to the anti-bonding molecular orbital of the CO ligand weakens the C≡O bond in the carbonyl. This prediction is in agreement with the observed increase in the C-O distance and the decrease in frequency of C-O valence vibrations observed in these complexes. In addition, B. can explain why the M-CO bond is rather stable – the bond order is between 1 and 2 – and has a low bond dipole moment. Other ligands capable of B. are CN^-, RCN and PF_3. Since B. stabilizes a negative formal charge on the central ion through charge transfer to the ligand, it can explain why the oxidation state of the central atom in complexes with strong B. is usually very low. For example, it is 0 in $Ni(CO)_4$ and $[Ni(CN)_4]^{4-}$, and in $[Co(CO)_4]^-$, it is -1. The bonding in ethene complexes, e.g. $PtCl_2C_2H_4$, is similar to that in metal carbonyls. The ethyne derivatives R-C≡C-R and nitriles, R-C≡N, also form π-complexes with transition metal ions. In addition, R. can also be used in describing bonding in electron excess compounds, e.g. in noble gas compounds.

Bacteriochlorin: see Porphyrins.

Bacteriochlorophyll: see Chlorophylls.

Bacteriocide: a substance which kills bacteria and is used as a drug, disinfectant, preservative (also for protection of wood, leather and textiles) and pesticide. B. are used to combat the bacterial pathogens of plant diseases and to prevent rotting of harvested products. Many fungicides used to protect plants also have bacteriocidal or bacteriostatic effects, for example, organomercury compounds, organotin compounds, copper oxygen chloride, chloranil, 8-hydroxyquinoline, diphenyl, 2-phenylphenol, antibiotics (e.g. chloramphenicol), etc. *Technofthalan* (*N*-[2',3'-dichlorophenyl]-3,4,5,6-tetrachlorophthalamic acid), *bronopol* (2-bromo-2-nitropropane-1,3-diol) and various quaternary ammonium compounds are used specifically against bacterial pathogens.

Bacteriorhodopsin: see Vitamin A.

Badger-Bauer rule: an empirical relationship relating the association enthalpy of an H-bond and the frequency shift of the X-H valence vibration in the infrared (see Infrared spectroscopy); according to the B., the relationship is linear so long as solvation interactions and steric hindrance can be excluded. This rule is only true within limits. It is most applicable when structurally similar systems are studied, where either the proton donor in the H bridges is the same while the acceptor varies, or vice versa.

Baeyer's tension hypothesis: an hypothesis concerning spatial structure and reactivity of cycloalkanes. A. von Bayer assumed that the cycloalkanes were planar. From the magnitude of the deviation of the ring angles from the tetrahedral angle (109° 28'),

he defined a *ring tension*, the *bond-angle* or *Bayer tension*, to explain the different thermodynamic stabilities of cycloalkanes with different ring sizes (the stabilities are derived from the heats of combustion). His relationship holds for cyclopropane, cyclobutane and cyclopentane, but not for cyclohexane or the larger cycloalkanes. The reason is that only cyclopropane is planar, as was predicted in 1890 by Sachse and 1918 by Mohr. The classical B. is therefore not applicable. The Bayer tension is small in all cycloalkanes, since even the angles in cyclobutane and cyclopentane are close to the tetrahedral value; however, together with the Pitzer tension (see Stereoisomerism, 2.1), it determines the stable conformations of small and normal rings. When transannular tension is added, these values determine the conformation of medium-sized rings also.

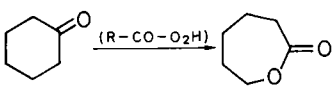
Baeyer tension: see Baeyer's tension hypothesis.

Baeyer test: a detection reaction for double bonds in organic compounds (see Alkenes); in the presence of double bonds, potassium permanganate is bleached.

Baeyer-Villinger oxidation: a method developed in 1899 for oxidation of ketones to carboxylic acid esters using peroxy acids, e.g. peracetic, perbenzoic or trifluoroperacetic acid:

$$R^1\text{–CO–}R^2 \xrightarrow{(R\text{–CO–}O_2H)} R^1\text{–CO–O}R^2$$

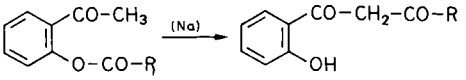
In the oxidation of cyclic ketones under these reaction conditions, lactones are formed:



Bagasse: the lignocellulose residue remaining after extraction of the juice from the sugar cane (*Saccharum officinale*). B. is used as a source of cellulose (2.5 t B. yields 1 t paper) and furfural.

Bakelite: international term for Phenol resins (see).

Baker-Venkataraman rearrangement: conversion of 2-acyloxyacetophenones to 1,3-diketones in the presence of basic condensing agents, such as sodium, sodium amide or sodium hydroxide, in benzene, ether or toluene:



The mechanism of the B. can be interpreted as an intramolecular ester condensation.

Baking: the production of aminosulfonic acids by dry heating (baking) of the sulfates of various aromatic amines to about 260-280 °C. Sulfanilic acid, for example, is made from aniline sulfate via sulfaminic acid as an intermediate:

$$C_6H_5\text{–}NH_2 \cdot H_2SO_4 \xrightarrow[-H_2O]{} C_6H_5\text{–NH–}SO_3H$$

$$\rightarrow HO_3S\text{–}C_6H_4\text{–}NH_2.$$

The method can be used to sulfonate aromatic amines without protecting the amino group. Today, the reaction is often carried out in high-boiling, inert organic solvents, such as 1,2-dichlorobenzene. At the boiling temperature of the solvent, the water is cleaved off and then separated.

Bake-on paints: paints based on acrylic, epoxide, phenol, melamine, urea, polyurethane and other resins, which harden alone or in combination at temperatures up to 250 °C. They can be colored by suitable pigments. The silicone resin B. (see Polysiloxanes) are very important. B. are very hard and stretch well; they are resistant to scratching, the weather and chemical effects.

BAL: same as Dimercaprol (see).

Balata: a coagulated latex from the tree *Mimusops balata*, which is very similar to gutta percha. Unlike natural rubber, it is hard, tough and only slightly elastic. Like rubber, B. can be vulcanized, and it is sometimes added to rubber mixtures. B. was used for drive belts, and de-resined B. is used for the outer layer of golf balls.

Ball and stick models: see Stereochemistry.

Balmer series: see Atomic spectroscopy.

Balsams: see Resins.

Bamford-Stevens reaction: a method for making diazoalkanes by alkaline cleavage of tosylhydrazones. These can be obtained by reaction of carbonyl compounds with tosylhydrazine:

$$R^1R^2C{=}O + H_2N\text{–NH–}SO_2\text{–}C_6H_4\text{–}CH_3 \xrightarrow[-H_2O]{} R^1R^2{=}N\text{–NH–}SO_2\text{–}C_6H_4\text{–}CH_3 \xrightarrow[-H_2O]{+OH^-}$$

$$R^1R^2\bar{C}\text{-}\overset{+}{N}{\equiv}N| + CH_3\text{–}C_6H_4\text{–}SO_2^-.$$

Band model: same as Energy band model (see).

Band spectrum: see Spectrum.

Barastu process: see Water softening.

Barban: see Carbanilate herbicides.

Barbital: see Barbitals.

Barbitals: 5,5-disubstituted barbituric acids. A nitrogen atom can also be alkylated, and the oxygen atom on C-2 can be replaced by a sulfur. Such compounds are called ***thiobarbitals***. B. are synthesized by condensation of dialkylmalonate esters or dialkylcyanoacetate esters with urea or urea derivatives. B. are weak acids, so that aqueous solutions of their salts with alkalies give a basic reaction. B. decompose in alkaline media due to ring opening of the heterocyclic ring by the hydroxide ions; usually the reaction occurs at C-4 or C-6. The end product is a monoacylurea.

Unsubstituted barbituric acid and 5-monosubstituted barbituric acids are not hypnotic. 5,5-Dimethylbarbituric acid has a very weak effect. Increasing the hydrophobicity of the compounds, e.g. by lengthening the chains of the alkyl groups or introduction of cycloaliphatic or aromatic groups, increases their pharmaceutical effects. The greatest activity is observed in compounds in which the sum of the numbers of carbon atoms in the two groups bound to C-5 is 6 to 8. Branched-chain compounds are more effective and less toxic than isomeric compounds with straight-chain substituents.