THE FACTS ON FILE DICTIONARY OF CHEMISTRY

DR. JOHN DAINTITH

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Edited by John Daintith



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The illustration on the jacket of this book is a micro-photograph of water molecules

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DICTIONARY of CHEMISTRY

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A

absolute alcohol Pure alcohol (ethanol).

absolute temperature Symbol: T A temperature defined by the relationship: $T = \theta + 273.15$

where θ is the Celsius temperature. The absolute scale of temperature was a fundamental scale based on Charles' law applied to an ideal gas:

 $V = V_0(1 + \alpha\theta)$

where V is the volume at temperature θ . V_0 the volume at 0, and α the thermal expansivity of the gas. At low pressures (when real gases show ideal behaviour) α has the value 1/273.15. Therefore, at 0 = -273.15 the volume of the gas theoretically becomes zero. In practice, of course, substances become solids at these temperatures. However, the extrapolation can be used for a scale of temperature on which -273.15°C corresponds to 0° (absolute zero). The scale is also known as the ideal-gas scale; on it temperature intervals were called degrees absolute (°A) or degrees Kelvin (°K), and were equal to the Celsius degree. It can be shown that the absolute temperature scale is identical to the thermodynamic temperature scale (on which the unit is the kelvin).

absolute zero The zero value of thermodynamic temperature; 0 kelvin or -273.15°C.

absorption A process in which a gas is taken up by a liquid or solid, or in which a liquid is taken up by a solid. In absorption, the substance absorbed goes into the bulk of the material. Solids that absorb gases or liquids often have a porous structure. The absorption of gases in solids is sometimes called sorption. Compare adsorption.

absorption indicator (adsorption indicator) An indicator used for titrations that involve a precipitation reaction.

The method depends upon the fact that at the equivalence point there is a change in the nature of the ions absorbed by the precipitate particles. Fluorescein - a fluorescent compound — is commonly used. For example, in the titration of sodium chloride solution with added silver nitrate, silver chloride is precipitated. Sodium ions and chloride ions are absorbed in the precipitate. At the end point, silver ions and nitrate ions are in slight excess and silver ions are then absorbed. If fluorescein is present, negative fluorescein ions absorb in preference to nitrate ions, producing a pink complex.

absorption spectrum See spectrum.

abundance 1. The relative amount of a given element amongst others; for example, the abundance of oxygen in the Earth's crust is approximately 50% by mass.

2. The amount of a nuclide (stable or radioactive) relative to other nuclides of the same element in a given sample. The *natural abundance* is the abundance of a nuclide as it occurs naturally. For instance, chlorine has two stable isotopes of masses 35 and 37. The abundance of ³⁵Cl is 75.5% and that of ³⁷Cl is 24.5%. For some elements the abundance of a particular nuclide depends on the source.

accelerator A catalyst added to increase the rate of a reaction.

acceptor The atom or group to which a pair of electrons is donated in a coordinate bond.

accumulator (secondary cell, storage battery) An electric cell or battery that can be charged by passing an electric current through it. The chemical reaction in the cell is reversible. When the cell begins to run down, current in the opposite direction will convert the reaction products back into their original forms. The most common example is the lead-acid accumulator, used in vehicle batteries.

acetal A type of organic compound formed by addition of an alcohol to an aldehyde. Addition of one alcohol molecule gives a hemiacetal. Further addition yield the full acetal. Similar reactions occur with ketones to produce hemiketals and ketals.

acetaldehyde See ethanal.

acetamide See ethanamide.

acetate See ethanoate.

acetic acid See ethanoic acid.

acetone See propanone.

acetylation See acylation.

acetyl chloride See ethanoyl chloride.

acetylene See ethyne.

acetyl group See ethanoyl group.

Acheson process See carbon.

acid A substance that gives rise to hydrogen ions (or H₃O⁺) when dissolved in water. An acid in solution will have a pH below 7. This definition does not take into account the competitive behaviour of acids in solvents and it refers only to aqueous systems. The Lowry-Brønsted theory defines an acid as a substance that exhibits a tendency to release a proton, and a base as a substance that tends to accept a proton. Thus, when an acid releases a proton, the ion formed is the conjugate base of the acid. Strong acids (e.g. HNO₃) react completely with water to give H₃O⁺, i.e. HNO3 is stronger than H3O+ and the conjugate base NO3 is weak. Weak acids (e.g. CH₃COOH and C₆H₅COOH) are only partly dissociated because H₃O⁺ is a stronger acid than the free acids and the ions CH3COO- and C₆H₅COO⁻ are moderately strong bases. See also Lewis acid.

acid anhydride A type of organic compound of general formula RCOO-

$$C = 0$$

Acid anhydride

COR', where R and R' are alkyl or aryl groups. They are prepared by reaction of an acyl halide with the sodium salt of a carboxylic acid, e.g.:

RCOCl + R'COO-Na⁺ → RCOO-COR' + NaCl

Like the acyl halides, they are very reactive acylating agents. Hydrolysis is to carboxylic acids:

 $RCOOCOR' + H_2O \rightarrow RCOOH + R'COOH$

See also acylation.

acid dyes The sodium salts of organic acids used in the dyeing of silks and wool. They are so called because they are applied from a bath acidified with dilute sulphuric or acetic acid.

acid halide See acyl halide.

acidic Having a tendency to release a proton or to accept an electron pair from a donor. In aqueous solutions the pH is a measure of the acidity, i.e. an acidic solution is one in which the concentration of H₃O⁺ exceeds that in pure water at the same temperature; i.e. the pH is lower than 7.

acidic hydrogen A hydrogen atom in a molecule that enters into a dissociation equilibrium when the molecule is dissolved in a solvent. For example, in acetic acid (CH₃COOH) the acidic hydrogen is the one on the carboxyl group, -COOH.

acidimetry Volumetric analysis or acidbase titration in which a standard solution of an acid is added to the unknown (base) solution plus the indicator. Alkalimetry is the converse, i.e. the base is in the burette.

acidity constant See dissociation constant.

acid salt (acidic salt) A salt in which there is only partial replacement of the acidic hydrogen of an acid by metal or other cations. For polybasic acids the formulae are of the type NaHSO4 hydrogensulphate) (sodium Na₃H(CO₃)₂.2H₂O (sodium sesquicarbonate). For monobasic acids such as HF the acid salts are of the form KHF2 (potassium hydrogen fluoride). Although the latter were at one time formulated as a normal salt plus excess acid (i.e. KF.HF) it is preferable to treat these as hydrogen-bonded systems of the type K + (F-H-F).

acid value A measure of the free acid present in fats, oils, resins, plasticizers, and solvents, defined as the number of milligrams of potassium hydroxide required to neutralize the free acids in one gram of the substance.

actinic radiation Radiation that can cause a chemical reaction; for example, ultraviolet radiation is actinic.

actinides See actinoids.

actinium A toxic radioactive metallic element that is the first member of the actinoid series. It occurs in minute quantities in uranium ores and has been used as a source of alpha particles. Symbol: Ac; m.p. 1050°C; b.p. 3200°C (calc.); r.d. 10.07 (calc.); p.n. 89; stablest isotope ²²⁷Ac (half-life 21.6 years).

actinoids (actinides) A group of 15 radioactive elements whose electronic configurations display filling of the 5f level. As with the lanthanoids, the first member, actinium, has no f electrons (Ac [Rn]6d¹7s²) but other members also show deviations from the smooth trend of f electron filling expected from simple considerations, e.g. thorium Th [Rn]6d²7s², berkelium Bk [Rn]5f⁸6d¹7s².

The actinoids are all radioactive and their chemistry is often extremely difficult to study. In general, artificial methods using high-energy bombardment are used to generate them. See also transuranic elements.

activated charcoal See charcoal.

activated complex The partially bonded system of atoms in the transition state of a chemical reaction.

activation energy Symbol: E The minimum energy a particle, molecule, etc., must acquire before it can react; i.e. the energy required to initiate a reaction regardless of whether the reaction is exothermic or endothermic. Activation energy is often represented as an energy barrier that must be overcome if a reaction is to take place. See Arrhenius equation.

active mass See mass action, law of.

activity Symbol: A The average number of atoms disintegrating per unit time in a radioactive substance.

acyclic Describing a compound that is not cyclic (does not contain a ring in its molecules).

acylation A reaction that introduces the acyl group (RCO-). Acylating agents are acyl halides (R.CO.X) and acid anhydrides (R.CO.O.CO.R), which react with such nucleophiles as H2O, ROH, NH₃, and RNH₂. In these compounds a hydrogen atom of a hydroxyl or amine group is replaced by the RCO- group. In acetylation the acetyl group (CH₃CO-) is used. In benzoylation the benzovl group (C₆H₅CO-) is used. Acylation is used to prepare crystalline derivatives of organic compounds to identify them (e.g. by melting point) and to protect -OH groups in synthetic reactions.

acyl anhydride See acid anhydride.

acyl group The group of atoms RCO-.



Acyl halide

acyl halide (acid halide) A type of organic compound of the general formula RCOX, where X is a halogen (acyl chloride, acyl bromide, etc.).

Acyl halides can be prepared by the reaction of carboxylic acid with a halogenating agent. Commonly, phosphorus halides are used (e.g. PCl₅) or a sulphur dihalide oxide (e.g. SOCl₂):

RCOOH + PCl₅ → RCOCl + POCl₃ + HCl

 $RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$

The acyl halides have irritating vapours and fume in moist air. They are very reactive to the hydrogen atom of compounds containing hydroxyl (-OH) or amine (-NH₂) groups. See acylation.

addition reaction A reaction in which additional atoms or groups of atoms are introduced into an unsaturated compound, such as an alkene or ketone. A simple example is the addition of bromine across the double bond in ethene:

 $H_2C:CH_2 + Br_2 \rightarrow BrH_2CCH_2Br$ Addition reactions can be induced either by electrophiles or by nucleophiles. See also electrophilic addition, nucleophilic addition.

addition polymerization See polymerization.

adduct See coordinate bond.

adiabatic change A change during which no energy enters or leaves the system.

In an adiabatic expansion of a gas, mechanical work is done by the gas as its volume increases and the gas temperature falls. For an ideal gas

undergoing a reversible adiabatic change it can be shown that

$$pV^{\gamma} = K_1$$

$$T^{\gamma}p^{1-\gamma} = K_2$$
and
$$TV^{\gamma-1} = K_3$$

where K_1 , K_2 , and K_3 are constants and γ is the ratio of the principal specific heat capacities.

Compare isothermal change.

adipic acid See hexanedioic acid.

adsorption A process in which a layer of atoms or molecules of one substance forms on the surface of a solid or liquid. All solid surfaces take up layers of gas from the surrounding atmosphere. The adsorbed layer may be held by chemical bonds (chemisorption) or by weaker van der Waals forces (physisorption). Compare absorption.

adsorption indicator See absorption indicator.

aerosol See sol.

afterdamp See firedamp.

air The mixture of gases that surrounds the Earth. The composition of dry air, by volume, is nitrogen 78.08% oxygen 20.95% argon 0.93%

carbon dioxide 0.03% neon 0.0018%

helium 0.0005% krypton 0.0001%

xenon 0.00001%

Air also contains a variable amount of water vapour, as well as dust, pollen, and small amounts of other gases.

air gas See producer gas.

alabaster A mineral form of gypsum (CaSO₄.2H₂O).

alanine See amino acids.

alcohol A type of organic compound of the general formula ROH, where R is a hydrocarbon group. Examples of simple

primary

secondary

tertiary

Alcohols

alcohols are methanol (CH3OH) and ethanol (C₂H₅OH).

Alcohols have the -OH group attached to a carbon atom that is not part of an aromatic ring. Thus, C₆H₅OH, in which the -OH group is attached to the ring, is a phenol. Phenylmethanol (C₆H₅C-H₂OH) does have the characteristic properties of alcohols.

Alcohols are classified according to the environment of the -C-OH grouping. If the carbon atom is attached to two hydrogen atoms, the compound is a primary alcohol. If the carbon atom is attached to one hydrogen atom and two other groups, it is a secondary alcohol.

If the carbon atom is attached to three other groups, it is a tertiary alcohol. Alcohols can be prepared by:

(1) Hydrolysis of haloalkanes using aqueous potassium hydroxide:

RI + OH - → ROH + I-

(2) Reduction of aldehydes by nascent hydrogen (from sodium amalgam in water):

RCHO + $2[H] \rightarrow RCH_2OH$

The main reactions are:

(1) Oxidation by potassium dichromate(VI) in sulphuric acid. Primary alcohols give aldehydes, which are further oxidized to carboxylic acids:

 $RCH_2OH \rightarrow RCHO \rightarrow RCOOH$ Secondary alcohols are oxidized to

(2) Formation of esters with acids. The reaction, which is reversible, is catalysed by H + ions:

ROH + R'COOH = R'COOR

(3) Dehydration over hot pumice (400°C) to alkenes:

 $RCH_2CH_2OH - H_2O \rightarrow RCH:CH_2$

(4) Reaction with sulphuric acid. Two types of reaction are possible. With excess acid at 160°C dehydration occurs to give an alkene:

 $RCH_2CH_2OH + H_2SO_4 \rightarrow H_2O +$ RCH₂CH₂.HSO₄

 $RCH_2CH_2.HSO_4 \rightarrow RCH:CH_2 + H_2SO_4$ With excess alcohol at 140°C an ether is formed:

 $2ROH \rightarrow ROR + H_2O$ See also acylation, haloalkane.

$$R-C = 0$$

Aldehyde

aldehyde A type of organic compound with the general formula RCHO, where the -CHO group (the aldehyde group) consists of a carbonyl group attached to a hydrogen atom. Simple examples of aldehydes are methanal (formaldehyde, HCHO) and ethanal (acetaldehyde, CH₃CHO).

Aldehydes are formed by oxidizing a primary alcohol. In the laboratory potassium dichromate(VI) is used in sulphuric acid. They can be further oxidized to carboxylic acids. Reduction (using a catalyst or nascent hydrogen from sodium amalgam in water) produces the parent alcohol.

Aldehydes undergo a number of reactions:

- (1) They act as reducing agents, being oxidized to carboxylic acids in the process. These reactions are used as tests for aldehydes using such reagents as Fehling's solution and Tollen's reagent (silver-mirror test).
- (2) They form addition compounds with hydrogen cyanide to give 'cyanohydrins'. For example, propanal gives 2-hydroxybutanonitrile:
- $C_2H_5CHO + HCN \rightarrow C_2H_5CH(OH)CN$ (3) They form addition compounds with the hydrogensulphate(IV) ion (HSO₃⁻): RCHO + HSO₃⁻ \rightarrow RCH(OH)(HSO₃) (4) They undergo condensation reactions with such compounds as hydrazine, hydroxylamine, and their derivatives.
- (5) With alcohols they form hemiacetals and acetals.
- (6) They polymerize readily. Polymethanal or methanal trimer can be formed from methanal depending on the conditions. Ethanal gives ethanal trimer or ethanal tetramer.

See also acetal, Cannizzaro reaction, condensation reaction, ketone.

aldohexose An aldose sugar with six carbon atoms. See sugar.

aldol See aldol reaction.

aldol reaction A reaction in which two molecules of aldehyde combine to give an aldol — i.e. a compound containing both aldehyde and alcohol functional groups. The reaction is base-catalysed; the reaction of ethanal refluxed with sodium hydroxide gives:

2CH₃CHO → CH₃CH(OH)CH₂CHO The mechanism is similar to that of the Claisen condensation: the first step is removal of a proton to give a carbanion, which subsequently attacks the carbon of the carbonyl group on the other molecule:

 $CH_3CHO + OH^- \rightarrow {}^-CH_2CHO + H_2O$

See also Claisen condensation.

aldopentose An aldose sugar with five carbon atoms. See sugar.

aldose A sugar containing an aldehyde (CHO) or potential aldehyde group. See sugar.

alicyclic compound An aliphatic cyclic compound, such as cyclohexane.

aliphatic compound An organic compound with properties similar to those of the alkanes, alkenes, and alkynes and their derivatives. Most aliphatic compounds have an open chain structure but some, such as cyclohexane and sucrose, have rings. The term is used in distinction to aromatic compounds, which are similar to benzene. Compare aromatic compound.

alkali A water-soluble strong base. Strictly the term refers to the hydroxides of the alkali metals (group I) only, but in common usage it refers to any soluble base. Thus borax solution may be described as mildly alkaline.

alkali metals (group I elements) A group of soft reactive metals, each representing the start of a new period in the periodic table and having an electronic configuration consisting of a noble-gas structure plus one outer electron. The alkali metals are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr).

The elements all easily form positive ions M^+ and consequently are highly reactive (particularly with any substrate that is oxidizing). As the group is descended there is a gradual decrease in ionization potential and an increase in the size of the atoms; the group shows several smooth trends which follow from this. For example, lithium reacts in a fairly controlled way with water, sodium

ignites, and potassium explodes. There is a general decrease in the following: melting points, heats of sublimation, lattice energy of salts, hydration energy of M⁺, ease of decomposition of nitrates and carbonates, and heat of formation of the "-ide" compounds (fluoride, hydridge, oxide, carbide, chloride).

Lithium has the smallest ion and therefore the highest charge/size ratio and is polarizing with a tendency towards covalent character in its bonding; the remaining elements form typical ionic compounds in which ionization, M+X-, is regarded as complete. The slightly anomalous position of lithium is illustrated by the similarity of its chemistry to that of magnesium. For example, lithium hydroxide is much less soluble than the hydroxides of the other group I elements; lithium perchlorate is soluble in several organic solvents. Because of the higher lattice energies associated with smaller ions lithium hydride and nitride are fairly stable compared to NaH which decomposes at 345°C. Na₂N, K₁N etc., are not obtained pure and decompose below room temperature.

The oxides also display the trend in properties as lithium forms M_2O with only traces of M_2O_2 , sodium forms M_2O_2 and at high temperatures and pressures MO_2 , potassium, rubidium, and caesium form M_2O_2 if oxygen is restricted but MO_2 if burnt in air. Hydrolysis of the oxides or direct reaction of the metal with water leads to the formation of the hydroxide ion.

Salts of the bases MOH are known for all acids and these are generally white crystalline solids. The ions M⁺ are hydrated in water and remain unchanged in most reactions of alkali metal salts.

Because of the ease of formation of the ions M^+ there are very few coordination compounds of the type ML_n^+ apart from solvated species of very low correlation times. The group I elements form a variety of organometallic compounds; the bonding in lithium alkyls and aryls is essentially covalent but the heavier elements form ionic compounds. Organo-alkali metal compounds — particularly the lithium

compounds — are widely used in synthetic organic chemistry.

Francium is formed only by radioactive decay and in nuclear reactions; all the isotopes of francium have short half-lives. The few chemical studies which have been carried out indicate that it would have similar properties to those of the other metals.

alkalimetry See acidimetry.

alkaline-earth metals (group II elements) A group of moderately reactive metals, harder and less volatile than the alkali metals. The term alkaline earth strictly refers to the oxides, but is often used loosely for the elements themselves. The electronic configurations are all those of a noble-gas structure with an additional two electrons in the outer s orbital. The elements are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). The group shows an increasing tendency to ionize to the divalent state M2+. The first member, beryllium has a much higher ionization potential than the others and the smallest atomic radius. Thus it has a high charge/size ratio and consequently the bonding in beryllium compounds is largely covalent. The chemistry of the heavier members of the group is largely that of divalent ions.

The group displays a typical trend towards metallic character as the group is descended. For example, beryllium hydroxide is amphoteric; magnesium hydroxide is almost insoluble in water and is slightly basic; calcium hydroxide is sparingly soluble and distinctly basic: and strontium and barium hydroxides are increasingly soluble in water and strongly basic. The group also displays a smooth trend in the solubilities of the sulphates (MgSO4 is soluble, CaSO4 sparingly soluble, and BaSO₄ very insoluble). The trend to increasing metallic character is also shown by the increase in thermal stabilities of the carbonates and nitrates with increasing relative atomic mass.

The elements all burn in air (beryllium

must be finely powdered) to give the oxide MO (covalent in the case of beryllium) and for barium the peroxide, BaO₂ in addition to BaO. The heavier oxides, CaO, SrO, and BaO, react with water to form hydroxides, M(OH)₂; magnesium oxide reacts only at high temperatures and beryllium oxide not at all. The metals Ca, Sr, and Ba all react readily with water to give the hydroxide:

 $M+2H_2O \rightarrow M^{2+}+2OH^-+H_2$ In contrast, magnesium requires dilute acids in order to react (to the salt plus hydrogen), and beryllium is resistant to acid attack. A similar trend is seen in the direct reaction of hydrogen: under mild conditions calcium, strontium, and barium give ionic hydrides, high pressures are required to form magnesium hydride, and beryllium hydride can not be prepared by direct combination.

Because of its higher polarizing power, beryllium forms a range of complexes in which the beryllium atom should be treated as an electron acceptor (i.e. the vacant p orbitals are being used). Complexes such as etherates, acetylethanoates, and the tetrafluoride (BeF42-) are formed, all of which are tetrahedral. In contrast Mg2+, Ca2+, Sr2+, and Ba2+ have poor acceptor properties and form only weak complexes, even with donors such as ammonia or edta. Magnesium forms Grignard reagents (RMgX), which are important in organic synthesis, and related compounds R2Mg.MgX2 and R₂Mg are known. The few organic compounds of Ca, Sr, and Ba are ionic. All isotopes of radium are radioactive and radium was once widely used for radiotherapy. The half-life of 226Ra (formed by decay of ²³⁸U) is 1600 years.

alkaloid One of a group of natural organic compounds found in plants. They contain oxygen and nitrogen atoms. Most are poisonous. Examples are strychnine and quinine.

alkane A type of hydrocarbon with general formula C_nH_{2n+2} . Alkanes are saturated compounds, containing no double or triple bonds. Methane (CH₄)

and ethane (C_2H_6) are typical examples. The alkanes are fairly unreactive (their former name, the *paraffins*, means 'small affinity'). In ultraviolet radiation they react with chlorine to give a mixture of substitution products. There are a number of ways of preparing alkanes:

(1) From a sodium salt of a carboxylic acid treated with sodalime:

RCOO⁻Na⁺ + NaOH → RH + Na₂CO₃
(2) By reduction of a haloalkane with nascent hydrogen from the action of ethanol on a zinc-copper couple:

 $RX + 2[H] \rightarrow RH + HX$

(3) By the Wurtz reaction — i.e. sodium in dry ether on a haloalkane:

 $2RX + 2Na \rightarrow 2NaX + RR$

(4) By the Kolbé electrolytic method:

RCOO- → RR

(5) By refluxing a haloalkane with magnesium in dry ether to form a Grignard reagent:

 $RI + Mg \rightarrow RMgI$ With acid this gives the alkane: $RMgI + H \rightarrow RH$

The main source of lower molecular weight alkanes is natural gas (for methane) and crude oil.

alkene A type of hydrocarbon with the formula C_nH_{2n} . The alkenes (formerly called *olefins*) are unsaturated compounds containing double carboncarbon bonds. They can be obtained from crude oil by cracking alkanes. Important examples are ethene (C_2H_4) and propene (C_3H_6), both of which are used in plastics production and as starting materials for the manufacture of other organic chemicals.

The methods of synthesizing alkenes

(1) The elimination of HBr from a haloalkane using an alcoholic solution of potassium hydroxide:

 $RCH_2CH_2Br + KOH \rightarrow KBr + H_2O + RCH_2CH_2$

(2) The dehydration of an alcohol by passing the vapour over hot pumice (400°C):

 $RCH_2CH_2OH \rightarrow RCH:CH_2 + H_2O$ The reactions of alkenes include:

(1) Hydrogenation using a catalyst (usually nickel at about 150°C):

RCH:CH₂ + H₂ → RCH₂CH₃

(2) Addition reactions with halogen acids to give haloalkanes:

RCH:CH₂ + HX \rightarrow RCH₂CH₂X The addition follows Markovnikoff's rule. (3) Addition reactions with halogens, e.g.

 $RCH:CH_2 + Br_2 \rightarrow RCHBrCH_2Br$

(4) Hydration using concentrated sulphuric acid, followed by dilution and warming:

 $RCH:CH_2 + H_2O \rightarrow RCH(OH)CH_3$

(5) Oxidation by cold potassium permanganate solutions to give diols:

RCH:CH₂ + H₂O + [O]
$$\rightarrow$$
 RCH(OH)CH₂OH

Ethene can be oxidized in air using a silver catalyst to the cyclic compound epoxy ethane (C_2H_4O) .

(6) Polymerization to polyethene (by the Ziegler or Phillips process).

See also oxo reaction, ozonolysis.

alkoxide An organic compound containing an ion of the type RO⁻, where R is an alkyl group. Alkoxides are made by the reaction of metallic sodium on an alcohol. Sodium ethoxide (C₂H₅O⁻Na⁺) is an example.

alkylbenzene A type of organic hydrocarbon containing one or more alkyl groups substituted onto a benzene ring. Methylbenzene (C₆H₅CH₃) and 1,3-dimethylbenzene are simple examples. Alkylbenzenes can be made by a Friedel-Crafts reaction or by the Fittig reaction. Industrially, large quantities of methylbenzene are made by the hydroforming of crude oil.

Substitution of alkylbenzenes can occur at the benzene ring. The alkyl group directs the substituent into the 2- or 4-position. Substitution of hydrogen atoms on the alkyl group can also occur.

alkyne A type of hydrocarbon with the general formula C_nH_{2n-2} . The alkynes are unsaturated compounds containing triple carbon-carbon bonds. The simplest member of the series is ethyne (C_2H_2) , which can be prepared by the action of water on calcium dicarbide.

The alkynes were formerly called the acetylenes.

 $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

In general, alkynes can be made by the cracking of alkanes or by the action of a hot alcoholic solution of potassium hydroxide on a dibromoalkane, for example:

 $BrCH_2CH_2Br + KOH \rightarrow KBr + CH_2:CHBr + H_2O$

CH₂:CHBr + H_2O CH₂:CHBr + KOH \rightarrow CHCH + KBr + H_2O

The main reactions of the alkynes are:

(1) Hydrogenation with a catalyst (usually nickel at about 150°C):

$$C_2H_2 + H_2 \rightarrow C_2H_4$$

 $C_2H_4 + H_2 \rightarrow C_2H_6$

(2) Addition reactions with halogen acids:

$$C_2H_2 + HI \rightarrow H_2C:CHI$$

 $H_2C:CHI + HI \rightarrow CH_3CHI_2$

(3) Addition of halogens; for example, with bromine in carbon tetrachloride:

 $C_2H_2 + Br_2 \rightarrow BrHC:CHBr$ $BrHC:CHBr + Br_2 \rightarrow Br_2HCCHBr_2$ (4) With dilute sulphuric acid at 60-80°C and mercury(II) catalyst, ethyne forms ethanal:

 $C_2H_2 + H_2O \rightarrow H_2C:C(OH)H$ This enol form converts to the aldehyde:

CH₁COH

(5) Ethyne polymerizes if passed through a hot tube to produce some benzene:

$$3C_2H_2 \rightarrow C_6H_6$$

(6) Ethyne forms dicarbides (acetylides) with ammoniacle solutions of copper(I) and silver(I) chlorides.

alkyl group A group obtained by removing a hydrogen atom from an alkane or other aliphatic hydrocarbon.

alkyl halide See haloalkane.

allotropy The ability of certain elements to exist in more than one physical form. Sulphur and phosphorus are the most common examples. Allotropy is more common in groups IV, V, and VI of the periodic table than in other groups. See also enantiotropy, monotropy.

alloy A mixture of two or more metals (e.g. bronze or brass) or of a metal with small amounts of non-metals, (e.g. steel).

Alloys may be completely homogeneous mixtures or may contain small particles of one phase in the other phase.

Alnico (Trademark) Any of a group of very hard brittle alloys used to make powerful permanent magnets. They contain nickel, aluminium, cobalt, and copper in various proportions. Iron, titanium, and niobium can also be present. They have a high remanence and coercive force.

alum A type of double salt. Alums are double sulphates obtained by crystallizing mixtures in the correct proportions. They have the general formulae:

M₂SO₄.M'₂(SO₄)₃.24H₂O Where M is a univalent metal or ion, and M' is a trivalent metal. Thus, aluminium potassium sulphate (called potash alum, or simply alum) is

K₂SO₄.Al₂(SO₄)₃.24H₂O

Aluminium ammonium sulphate (called ammonium alum) is

 $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$

The name 'alum' originally came from the presence of Al³⁺ as the trivalent ion, but is also applied to other salts containing trivalent ions, thus:

Chromium(III) potassium sulphate (chrome alum)

K₂SO₄.Cr₂(SO₄)₃.24H₂O

alumina See aluminium oxide.

aluminate See aluminium hydroxide.

aluminium A soft moderately reactive metal; the second element in group III of the periodic table. It has the electronic structure of neon plus three additional outer electrons. There are numerous minerals of aluminium; it is the most common metallic element in the Earth's crust (8.1% by weight) and the third in order of abundance. Commercially important minerals are bauxite (hydrated Al₂O₃), corundum (anhydrous Al₂O₃), cryolite (Na₃AlF₆), and clays and mica (aluminosilicates). The metal

is produced on a massive scale by the Hall-Heroult method in which alumina. a non-electrolyte, is dissolved in molten cryolite and electrolysed. The bauxite contains iron, which would contaminate the product, so the bauxite is dissolved in hot alkali, the iron oxide is removed by filtration, and the pure alumina then precipitated by acidification. Molten aluminium is tapped off from the base of the cell and oxygen evolved at the anode. The aluminium atom is much bigger than boron and its ionization potential is not particularly high. Consequently aluminium forms positive ions Al3+. However, it also has non-metallic chemical properties. Thus, it is amphoteric and also has a number of covalently bonded compounds.

Unlike boron, aluminium does not form a vast range of hydrides — AlH₃ and Al₂H₆ may exist at low pressures, and the only stable hydride, (AlH₃)_n, must be prepared by reduction of aluminium trichloride. The ion AlH₄ is widely used in the form as LiAlH₄ as a vigorous reducing agent.

The reaction of aluminium metal with oxygen is very exothermic but at ordinary temperatures an impervious film of the oxide protects the metal from further attack. This oxide film also protects aluminium from oxidizing acids. There is only one oxide, Al₂O₃ (alumina), but a variety of polymorphs and hydrates are known. It is relatively inert and has a high melting point, and for this reason is widely used as a furnace lining and for general refractory brick. Aluminium metal will react with alkalis releasing hydrogen and producing initially Al(OH)₃ then Al(OH)₄.

Aluminium reacts readily with the halogens; in the case of chlorine thin sheets will enflame. The fluoride has a high melting point (1290°C) and is ionic. The other halides are dimers in the vapour phase (two halogen bridges). Aluminium also forms a sulphide (Al₂S₃), nitride (AlN), and carbide (Al₄C), the latter two at extremely high temperatures.

Because of aluminium's ability to expand its coordination number and tendency

towards covalence it forms a variety of complexes such as AlF_6^{2-} and $AlCl_4^{-}$. A number of very reactive aluminium alkyls are also known, some of which are important as polymerization catalysts.

Symbol: Al; m.p. 659.8°C; b.p. 1800°C; r.d. 2.702; p.n. 13; r.a.m. 26.97.

aluminium acetate (aluminium ethanoate, Al(OOCCH₃)₃) A white solid soluble in water. It is usually obtained as the dibasic salt, basic aluminium ethanoate (Al(OH)(C₂H₂O₂)₂). It is prepared by dissolving aluminium hydroxide in ethanoic acid and is used extensively as a mordant in dyeing and as a size for paper and cardboard products. The solution is hydrolysed and contains various complex aluminium-hydroxyl species and colloidal aluminium hydroxide.

aluminium bromide (AlBr₃) A white solid soluble in water and many organic solvents.

aluminium chloride (AlCl₃) A white covalent solid that fumes in moist air:

 $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$ It is prepared by heating aluminium in dry chlorine or dry hydrogen chloride. Vapour-density measurements show that its structure is a dimer; it consists of Al_2Cl_6 molecules in the vapour. The $AlCl_3$ structure would be electron deficient. Aluminium chloride is used in Friedel-Crafts reactions in organic preparations.

aluminium fluoride (AlF₃) A white crystalline solid that is slightly soluble in water but insoluble in most organic solvents. Its primary use is as an additive to the cryolite (Na₃AlF₆) electrolyte in the production of aluminium

aluminium hydroxide (Al(OH)₃) A white powder prepared as a colourless gelatinous precipitate by adding ammonia solution or a small amount of sodium hydroxide solution to a solution of an aluminium salt. It is an amphoteric hydroxide. It is used as a foaming agent

in fire extinguishers and as a mordant in dyeing.

Its amphoteric nature causes it to dissolve in excess sodium hydroxide solution to form the *aluminate* ion.

 $Al(H_2O)_3(OH)_3 + OH^- \rightarrow Al(H_2O)_2(OH)_4^- + H_2O$

No aluminium carbonate is produced since solutions of carbonates are sufficiently alkaline to precipitate aluminium hydroxide from solutions of aluminium salts. When precipitating, aluminium hydroxide readily absorbs coloured matter from dyes to form lakes.

aluminium nitrate (Al(NO₃)₃,9H₂O) A hydrated white crystalline solid prepared by dissolving freshly prepared aluminium hydroxide in nitric acid. It cannot be prepared by the action of dilute nitric acid on aluminium since the metal is rendered passive.

aluminium oxide (alumina, Al₂O₃) A white powder that is almost insoluble in water. Because of its amphoteric nature it will react with both acids and alkalis. Aluminium oxide occurs naturally as bauxite, corundum, and white sapphire; it is manufactured by heating aluminium hydroxide. It is used in the extraction by electrolysis of aluminium, as an abrasive (corundum), in furnace linings (because of its refractory properties), and as a catalyst (e.g. in the dehydration of alcohols).

aluminium potassium sulphate (potash alum, Al₂(SO₄)₃.K₂SO₄.24H₂O, AlK(SO₄)₂.12H₂O) A white solid, soluble in water but insoluble in alcohol, prepared by mixing equimolecular quantities of solutions of ammonium and aluminium sulphate followed by crystallization. It is used as a mordant for dyes, as a waterproofing agent, and as a tanning additive.

aluminium sulphate (Al₂(SO₄)₃.18H₂O) A white crystalline solid. It is used as a size for paper, a precipitating agent in sewage treatment, a foaming agent in fire control, and as a fireproofing agent. Its solutions are acidic by hydrolysis,

aluminium trimethyl

containing such species as $Al(H_2O)_5$ - $(OH)^{2+}$.

aluminium trimethyl See trimethylaluminium.

amalgam An alloy of mercury with one or more other metals. Amalgams may be liquid or solid. An amalgam of sodium (Na/Hg) with water is used as a source of nascent hydrogen.

americium A highly toxic radioactive silvery element of the actinoid series of metals. A transuranic element, it is not found naturally on Earth but is synthesized from plutonium. Americium-241 has been used in gamma-ray radiography.

Symbol: Am; m.p. 994°C; b.p. 2607°C; r.d. 13.67; p.n. 95; stablest isotope 243 Am (half-life 7.4×10^3 years).

amide A type of organic compound of general formula RCONH₂. Amides are white solids, which can be formed by the partial dehydration of the ammonium salt of a carboxylic acid:

RCOO $^{-}$ NH₄ $^{+}$ - H₂O \rightarrow RCONH₂ Glacial acetic acid can be used as the dehydrating agent.

Reactions of amides include:

(1) Reaction with hot acids to give carboxylic acids:

 $RCONH_2 + HCl + H_2O \rightarrow RCOOH + NH_4Cl$

(2) Reaction with nitrous acid to give carboxylic acids and nitrogen:

 $RCONH_2 + HNO_2 \rightarrow RCOOH + N_2 + H_2O$

(3) Dehydration by phosphorus(V) oxide to give a nitrile:

RCONH₂ - H₂O \rightarrow RCN See also Hofmann degradation.

amine A compound containing a nitrogen atom bound to hydrogen atoms or hydrocarbon groups. They have the general formula R₃N, where R can be hydrogen. Amines can be prepared by reduction of amides or nitro compounds. They are basic, forming the ion R₃NH⁺.

amino acids Derivatives of carboxylic

primary

Amines

acids in which a hydrogen atom in an aliphatic acid has been replaced by an amino group. Thus, from ethanoic acid, the amino acid 2-aminoethanoic acid (glycine) is formed. All are white, crystalline, soluble in water, and with the sole exception of the simplest member, all are optically active.

In the body the various proteins are assembled from the necessary amino acids and it is important therefore that all the amino acids should be present in sufficient quantities. In man, twelve of the twenty amino acids can be