

DICTIONARY OF ANALYTICAL CHEMISTRY

Edited
by
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Preface

This dictionary includes the most frequently used terms which have been carefully selected from the various fields of analytical chemistry such as spectroscopy, volumetric Analysis, Gravimetric Analysis, Electroanalytical Analysis, Qualitative Analysis etc.

Every attempt has been carefully made to write the entries in a clear and lucid style to provide both straight forward definitions and invaluable background information. At some appropriate places, line diagrams have been included whenever the meaning of a word can be best understood by means of a diagram.

This dictionary will be of immense value to undergraduate and post-graduate chemistry students. It will be also of value to the students of analytical chemistry, biochemistry, medicine, pharmacy and others studying or working in related fields.

When a dictionary of this kind is being compiled, it becomes essential to draw upon the work of many authorities and seek the advice of colleagues to all of whom the editors are deeply indebted.

Finally, the editors express their sincere thanks to the publishers and printer for printing this book promptly.

All comments from users on omissions or shortcomings will be most welcome.

EDITORS

A

Abel Tester. A laboratory instrument used in testing the flash point of kerosine and other volatile oils having flash points below 120°F (49°C); the oil is contained in a closed cup which is heated by a fixed flame below and a movable flame above.

Absolute Gravity. Density or specific gravity of a fluid reduced to standard conditions; for example, with gases, to 760 mmHg pressure and 0°C temperature. Also known as absolute density.

Absorbance. The common logarithm of the reciprocal of the transmittance of a pure solvent. Also known as absorbancy; extinction.

Absorbancy. See absorbance.

Absorbency Index. See absorptivity.

Absorber. Equipment in which a gas is absorbed by contact with a liquid.

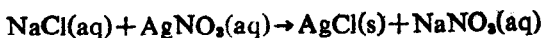
Absorptiometer

1. An instrument equipped with a filter system or other simple dispersing system to measure the absorption of nearly monochromatic radiation in the visible range by a gas or a liquid, and so determine the concentration of the absorbing constituents in the gas or liquid.
2. A device for regulating the thickness of a liquid in spectrophotometry.

Absorptiometric Analysis. Chemical analysis of a gas or a liquid by measurement of the peak electromagnetic absorption wavelengths that are unique to a specific material or element.

Absorption Edge. The wavelength corresponding to a discontinuity in the variation of the absorption coefficient of a substance with the wavelength of the radiation. Also known as absorption limit.

Absorption Indicator. A type of indicator used in reactions that involve precipitation. The yellow dye fluorescein is a common example, used for the reaction



As silver nitrate solution is added to the sodium chloride, silver chloride precipitates. As long as Cl^- ions are in excess, they adsorb on the precipitate particles. At the end point, no Cl^- ions are left in solution and negative fluorescein ions are then adsorbed, giving a pink colour to the precipitate.

Absorption Limit. See absorption edge.

Absorption Line. A minute range of wavelength or frequency in the electromagnetic spectrum within which radiant energy is absorbed by the medium through which it is passing.

Absorption Peak. A wavelength of maximum electromagnetic absorption by a chemical sample; used to identify specific elements, radicals, or compounds.

Absorption Plant. A facility to recover the condensable portion of natural or refinery gas.

Absorption Spectrophotometer. An instrument used to measure the relative intensity of absorption spectral lines and bands. Also known as difference spectrophotometer.

Absorption Spectroscopy. The study of spectra obtained by the passage of radiant energy from a continuous source through a cooler, selectively absorbing medium.

Absorption Spectrum. The array of absorption lines and absorption bands which results from the passage of radiant energy from a continuous source through a cooler, selectively absorbing medium.

Absorption Tube. A tube filled with a solid absorbent and used to absorb gases and vapors.

Absorptive Power. See absorptivity.

Absorptivity. The constant a in the Beer's law relation $A=abc$, where A is the absorbance, b the path length, and c the concentration of solution. Also known as absorptive power. Formerly known as absorbency index; absorption constant; extinction coefficient.

Accelofilter. A filtration device that uses a vacuum or pressure to draw or force the liquid through the filter to increase the rate of filtration.

Acetanilide. An odorless compound in the form of white, shining, crystalline leaflets or a white, crystalline powder with a melting point of $114-116^{\circ}\text{C}$; soluble in hot water, alcohol, ether, chloroform, acetone, glycerol and benzene; used as a rubber accelerator, in the manufacture of dyestuffs and intermediates, as a precursor in penicillin manufacture, and as a painkiller. Also known as *N*-phenylacetamide.

Acetoacetate. A salt which contains the $\text{CH}_3\text{COCH}_2\text{COO}$ radical; derived from acetoacetic acid.

Acetolysis. Decomposition of an organic molecule through the action of acetic acid or acetic anhydride.

Acetone Number. A ratio used to estimate the degree of polymerization of materials such as drying oils; it is the weight in grams of acetone added to 100 grams of a drying oil to cause an insoluble phase to form.

Acetone-sodium Bisulfite $(CH_3)_2C(OH)SO_2Na$. Crystals that have a slight sulfur dioxide odor and slightly fatty feel; freely soluble in water, decomposed by acids; used in photography and in textile dyeing and printing. Also known as acetone sulfite; 2-hydroxy-2 propanesulfonic acid sodium salt; sodium-acetone bisulfite.

Acetylating Agent. A reagent, such as acetic anhydride, capable of bonding an acetyl group onto an organic molecule.

Acetyllation. The process of bonding an acetyl group onto an organic molecule.

Acetyl Bromide CH_3COBr . A colourless, fuming liquid with a boiling point of $81^\circ C$; soluble in ether, chloroform, and benzene; used in organic synthesis and dye manufacture.

Acetyl Chloride CH_3COCl . A colourless, fuming liquid with a boiling point of $51-52^\circ C$; soluble in ether, acetone, and acetic acid; used in organic synthesis, and in the manufacture of dyestuffs and pharmaceuticals. Also known as ethanoyl chloride.

Acetyl Number. A measure of free hydroxyl groups in fats or oils determined by the amount of potassium hydroxide used to neutralize the acetic acid formed by saponification of acetylated fat or oil.

Acetyl Value. The number of milligrams of potassium hydroxide required for neutralization of acetic acid obtained by the saponification of one gram of acetylated fat or oil sample. Acetylation is carried out by boiling the sample with an equal amount of acetic anhydride, washing and drying. Saponification values on the acetylated and on untreated fat are determined. From the results the acetyl value is calculated. It is a measure of the number of free hydroxyl groups in the fat or oil.

Achromatic Indicators. Substances which give a grey end-point and generally find application in the titration of turbid liquids.

Acid-base Equilibrium. The condition when acidic and basic ions in a solution exactly neutralize each other; that is, the pH is 7.

Acid-base Indicator. A substance, a weak acid or weak base, which has a different colour in acid or base solution. The colour change is due to a marked difference in colour between the undissociated and ionic forms. For a good indicator the colour change must occur between narrow limits of pH, e.g. methyl orange is red at pH 3.1 and change to yellow at pH 4.4.

Acid Calcium Phosphate. See calcium phosphate.

Acid Cell. An electrolytic cell whose electrolyte is an acid.

Acid Chloride. A compound containing the radical -COCl ; an example is benzoyl chloride.

Acid Conductor. A vessel designed for refortification of hydrolyzed acid by heating and evaporation of water, or sometimes by distillation of water under partial vacuum.

Acid Dye. Any of a group of sodium salts of sulfonic and carboxylic acids used to dye natural and synthetic fibres, leather, and paper.

Acid Heat Test. The determination of degree of unsaturation of organic compounds by reacting with sulfuric acid and measuring the heat of reaction.

Acidic Titrant. An acid solution of known concentration used to determine the basicity of another solution by titration.

Acidification. Addition of an acid to a solution until the pH falls below 7.

Acidimeter. An apparatus or a standard solution used to determine the amount of acid in a sample.

Acidimetry. The titration of an acid with a standard solution of base.

Acidity. The state of being acid.

Acidity Coefficient. The ratio of the oxygen content of the bases in a rock to the oxygen content in the silica. Also known as oxygen ratio.

Acid Number. See acid value.

Acidolysis. A chemical reaction involving the decomposition of a molecule, with the addition of the elements of an acid to the molecule; the reaction is comparable to hydrolysis or alcoholysis, in which water or alcohol, respectively, is used in place of the acid. Also known as acyl exchange.

Acid Value. The number of milligrams of potassium hydroxide required to neutralize the free acids present in one gram of oil, fat, or wax. The determination is made by titrating the sample in hot 95% ethyl alcohol using phenolphthalein as indicator.

Acidimetry. The determination of the concentration of acid solutions or of the quantity of acid in a sample or mixture. This is usually done by titration with a solution of base of known strength (standard solution); an indicator is used to establish the end point.

Acree's Reaction. A test for protein in which a violet ring appears when concentrated sulfuric acid is introduced below a mixture of the unknown solution and a formaldehyde solution containing a trace of ferric chloride.

Acridine Orange. A dye with an affinity for nucleic acids; the complexes of nucleic acid and dye fluoresce orange with RNA and green with DNA when observed in the fluorescence microscope.

Acrolein Test. A test for the presence of glycerin or fats; a sample is heated with potassium bisulfate, and acrolein is released if the test is positive.

Action chemistry. A branch of chemistry concerned with chemical reactions produced by light or other radiation.

Activated Complex. An energetically excited state which is intermediate between reactants and products in a chemical reaction.

Activation. Treatment of a substance by heat, radiation, or activating reagent to produce a more complete or rapid chemical or physical change.

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

Activation Energy. The energy in excess over the ground state, which must be added to an atomic or molecular system to allow a particular process to take place.

Addition Reaction. A type of reaction of unsaturated hydrocarbons with hydrogen, halogens, halogen acids, and other reagents, so that no change in valency is observed and the organic compound forms a more complex one.

Adiabatic Calorimeter. An instrument used to study chemical reactions which have a minimum loss of heat.

Adiabatic Flame Temperature. The highest possible temperature of combustion obtained under the conditions that the burning occurs in an adiabatic vessel, that it is complete, and that dissociation does not occur.

Adsorbate. A solid, liquid, or gas which is adsorbed as molecules, atoms, or ions by such substances as charcoal, silica, metals, water and mercury.

Adsorbent. A solid or liquid that adsorbs other substances; for example, charcoal, silica, metals, water, and mercury.

Adsorption. The surface retention of solid, liquid, or gas molecules, atoms, or ions by a solid or liquid, as opposed to absorption, the penetration of substances into the bulk of the solid or liquid.

Adsorption Chromatography. Separation of a chemical mixture (gas or liquid) by passing it over an adsorbent bed which adsorbs different compounds at different rates.

Adsorption Indicator. An indicate which functions by adsorption on the surface of a precipitate. Thus in precipitating AgCl in the presence of excess Cl^- the surface has a layer of Cl^- and is negatively charged; in the presence of the indicator fluorescein the indicator is in solution. As soon as there is excess of Ag^+ the precipitate takes on a positive charge and the presence of the fluorescein anion as counter ion gives the precipitate a pinked red colour.

Adsorption Isohar. A graph showing how adsorption varies with some parameter, such as temperature, while holding pressure constant.

Adsorption Isotherm. The relationship between the gas pressure p and the amount w , in grams, of a gas or vapor taken up per gram of solid at a constant temperature.

AES. Auger electron spectroscopy.

Affinity Chromatography. A chromatographic technique that utilizes the ability of biological molecules to bend to certain ligands specifically and reversibly; used in protein biochemistry.

Aggressive Carbon Dioxide. The carbon dioxide dissolved in water in excess of the amount required to precipitate a specified concentration of calcium ions as calcium carbonate; used as a measure of the corrosivity and scaling properties of water.

Air Line. Lines in a spectrum due to the excitation of air molecules by spark discharges, and not ordinarily present in arc discharges.

Air Shower. See cosmic-ray shower.

Albite Law. A rule specifying the orientation of alternating lamellae in multiple twin feldspar crystals; the twinning plane is brachypinacoid and is common in albite.

Alignment. A population $p(m)$ of the $2I+1$ orientational substates of a nucleus; $m = -I$ to $+I$, such that $p(m) = p(-m)$.

Alkalescence. The property of a substance that is alkaline, that is, having a pH greater than 7.

Alkali. A hydroxide of one of the alkali metals. Also used for such substances as CaO , Ca(OH)_2 , Na_2CO_3 , which give an alkaline solution ($\text{pH} < 7$) in water. In aqueous solution the term alkali is virtually synonymous with the term base.

Alkali Blue. The sodium salt of triphenylrosanilinesulfonic acid; used as an indicator.

Alkalimeter.

1. An apparatus for measuring the quantity of alkali in a solid or liquid.
2. An apparatus for measuring the quantity of carbon dioxide formed in a reaction.

Alkalimetry. Quantitative measurement of the concentration of bases or the quantity of one free base in a solution; techniques include titration and other analytical methods.

Alkaline

1. Having properties of an alkali.
2. Having a pH greater than 7.

Alkaloid Reagents. Reagents, most of which are acids with complex anions, which give precipitates with alkaloids. The alkaloid reagents include chloroplatinic, phosphotungstic, phosphomolybdic, cyanoferrate, tannic, picric and sulphosalicylic acids, and potassium iodomercurate(II). They also precipitate proteins.

Alkalometry. The measurement of the quantity of alkaloids present in a substance.

Allihn Condenser. A condenser whose condensing surface is a series of interconnected glass bulbs.

Allochromatic Crystal. A crystal having photoconductive properties due to the presence of small particles within it.

Allomerism. A constancy in crystal form in spite of a variation in chemical composition.

Allotropy. The assumption by an element or other substance of two or more different forms or structures which are most frequently stable in different temperature ranges, such as different crystal-line forms of carbon as charcoal, graphite, or diamond. Also known as allotriomorphism; allotropism.

Alpha Decay. A radioactive transformation in which an alpha particle is emitted by a nuclide.

Alpha Emission. Ejection of alpha particles from the atom's nucleus.

Alpha-naphthol Test. A biochemical test to detect the presence of carbohydrates in solution, also known as Molisch's test (after the Austrian chemist H. Molisch (1856—1937), who devised it). A small amount of alcoholic alpha-naphthol is mixed with the test solution and concentrated sulphuric acid is poured slowly down the side of the test tube. A positive reaction is indicated by the formation of a violet ring at the junction of the two liquids.

Alpha-particle Scattering. Deviation at various angles of a stream of alpha particles passing through a foil of material.

Aluminate. A negative ion usually assigned the formula AlO_2^- and derived from aluminium hydroxide.

Aluminon $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_9$. A yellowish-brown, glassy powder that is freely soluble in water; used for the detection and calorimetric

estimation of aluminium in foods, water, and tissues, and as a pharyngeal aerosol spray. Also known as aurintricarboxylic acid triammonium salt.

S-(Z-aminoethyl) Isothiuronium Bromide Hydrobromide $C_3H_{11}Br_2N_3S$. Hygroscopic crystals with a melting point of $194-195^\circ\text{C}$; used as a radioprotective agent. Abbreviated AET.

Ammoniacal. Pertaining to ammonia or its properties. Also known as ammoniac.

Ammonia Water. A water solution of ammonia; a clear colourless liquid that is basic because of dissociation of NH_4OH to produce hydroxide ions; used as a reagent, solvent, and neutralizing agent.

Amperometric Titration. A method of analysis in which current flowing through a cell is plotted against added titrant. There are sharp breaks in the curves at the end points.

Amperometry. Chemical analysis by techniques which involve measuring electric currents.

Analysis. The identification of a substance or of the components in a mixture of substances is termed qualitative analysis. Analysis of inorganic substances is carried out by various physical methods; e.g. metals are analysed by spark spectra, mixtures may be analysed by ultra-violet or infrared spectroscopy, or by identification of X-ray powder patterns. Mixtures were formerly analysed by separations based on the different solubilities of various salts of cations, the anions most commonly used being chloride, sulphide, hydroxide and carbonate. However, this method is now little used. Teaching and modern chemical analysis is carried out using various organic reagents which are more or less specific for a given metal (see, e.g., aluminon, cupferron, magneson). Organic qualitative analysis is carried out by identification of the type of compound by physical methods or by specific reactions followed by complete identification by preparation of derivatives or by physical

methods. The physical methods most used are ultraviolet, infrared, or nuclear magnetic resonance spectroscopy, mass spectrometry, or molecular weight determination. Chromatography is much used.

Quantitative analysis is the estimation of the amount of element or group present in a mixture or compound. This is done by various methods, in volumetric analysis a titration, in gravimetric analysis a precipitation followed by a weighing, in colorimetric analysis the estimation of a coloured species. Other quantitative methods include infrared spectroscopy, estimation of the opalescence of a precipitate (turbidimetry, nephelometry and fluorimetry), estimation of optical rotation, electrolytic decomposition, potentiometric, conductometric and amperometric titrations, and polarography. Using the appropriate methods analysis can be carried out on almost any quantity of material. Organic quantitative analysis is generally carried out by physical methods or by conversion to known derivatives which can be estimated by weighing or by titration.

Analytical Chemistry. The subdivision of chemistry concerned with identification of materials (qualitative analysis) and with determination of the percentage composition of mixtures or the constituents of a pure compound (quantitative analysis). The gravimetric and volumetric (or "wet") methods (precipitation, titration, and solvent extraction) are still used for routine work; indeed, new titration methods have been introduced, e.g., cryoscopic, pressure metric (for reactions that produce a gaseous product), redox methods, and use of a fluoride-sensitive electrode. However, faster and more accurate techniques (collectively called instrumental) have been developed in the last few decades. Among these are infrared, ultraviolet, and x-ray spectroscopy, where the presence and amount of a metallic element is indicated by lines in its emission or absorption spectrum; colorimetry, by which the percentage of a

substance in solution is determined by the intensity of its colour; chromatography of various types by which the components of a liquid or gaseous mixture are determined by passing it through a column of porous material, or on thin layers of finely divided solids; separation of mixtures in ion-exchange columns; and radioactive tracer analysis. Optical and electron microscopy, mass spectrometry, microanalysis, nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) spectroscopy all fall within the area of analytical chemistry. See also spectroscopy, nuclear magnetic resonance, NQR spectroscopy, chromatography.

Analysis. The determination of the composition of a substance.

Analyte. The sample being analyzed.

Analytical Chemistry. The branch of chemistry dealing with techniques which yield any type of information about chemical systems.

Analytical Distillation. Precise resolution of a volatile liquid mixture into its components; the mixture is vaporized by heat or vacuum, and the vaporized components are recondensed into liquids at their respective boiling points.

Analytical Extraction. Precise transfer of one or more components of a mixture (liquid to liquid, gas to liquid, solid to liquid) by contacting the mixture with a solvent in which the component of interest is preferentially soluble.

Analyzing Power. In a nuclear scattering process, a measure of the effect on scattering cross sections of changes in the polarization of the beam or target nuclei.

Andrews Titration. An important titration for the estimation of reducing agents. The reducing agent is dissolved in concentrated hydrochloric acid and titrated with potassium iodate(V) solution. A drop of carbon tetrachloride is added to the solution and the end point is indicated by the disappearance of the iodine colour from this layer. The reducing agent is